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A SYSTEMATIC HANDBOOK
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VOLUMETRIC ANALYSIS.

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A

SYSTEMATIC HANDBOOK

OF

VOLUMETRIC ANALYSIS;

OR,

THE QUANTITATIVE ESTIMATION OF CHEMICAL SUBSTANCES BY MEASURE, APPLIED TO LIQUIDS, SOLIDS, AND GASES.

ADAPTED TO THE REQUIREMENTS OF PURE CHEMICAL RESEARCH,
PATHOLOGICAL CHEMISTRY, PHARMACY, METALLURGY, MANUFACTURING
CHEMISTRY, PHOTOGRAPHY, ETC., AND FOR THE VALUATION
OF SUBSTANCES USED IN COMMERCE, AGRICULTURE, AND THE ARTS.

BY

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PREFACE.

The five years which have elapsed since the publication of the second edition of this work, have resulted in the production of some new methods in Volumetric Analysis, together with the verification and improvement of those previously in use. I have endeavoured to embody in the present edition all such novelties and modifications as experiment have proved to be worthy of notice.

The book has been out of print nearly two years, owing to lack of time and the pressure of other matters, so that the necessary experiments for verification of results could not be carried out. I regret that there is still much to be done in the minute examination of individual processes, for it is only by careful detailed investigation of methods that their merits or demerits can be established.

The important sections on the Analysis of Potable Waters and Sewage, §§ 76, 77, 78, originally contributed to the second edition by Mr. W. Thorp, B.Sc., late principal assistant chemist to the Royal Commission on the Pollution of Rivers, have been thoroughly revised, and considerably augmented, by that gentleman.

This monograph on the analysis of waters by Drs. Frankland and Armstrong's system, is a special feature, and, I believe, will be found well worthy the attention of all chemists, and others interested in the sanitary aspects of water analysis; no pains have been spared by Mr. Thorp in this matter, and his intimate practical acquaintance with the subject, constitutes him one of the chief authorities in this branch of analysis.

Professor M^cLeod has also kindly revised his original contribution on the analysis of gases; it is, however, hardly necessary to say, that the admirably clear description of methods, together with the illustrations given by him in the second edition, needed very little improvement. The only regret I desire to express is that Professor M^cLeod, who has done so much for the advancement of gas analysis, has, with characteristic modesty, said so little about his own apparatus and improvements in this particular department of analysis.

I have further to thank Mr. W. Thorp for his kindness in revising the proof sheets before going to press. I trust that the errata to be discovered will be few and unimportant.

FRANCIS SUTTON.

NORWICH,
September, 1876.

CONTENTS.

PART I.

Sect. Page
1. General Principles 1
2. The Balance 4
3. Volumetric Analysis without Weights . . . 4
4. Volumetric Analysis without Burettes 5
5. The Burette 5
6. The Pipette 12
7. The Measuring Flasks 13
8. The Correct Reading of Graduated Instruments . . 14
9. The Weights and Measures to be adopted in Volumetric Analysis 16
10. Preparation of Normal Solutions 20
11. Direct and Indirect Processes of Analysis . . 26

PART II.

12. Alkalimetry and Acidimetry 28
13. Indicators 28
14. Normal Alkaline and Acid Solutions . . . 31
15. Correction of Abnormal Solutions 34
16. Titration of Alkalies and Acids 37
17. Ammonia 40
18. Nitrogenous Substances 43
19. Table for the Systematic Analysis of Acids, Alkalies, and Alkaline Earths 44
20. Alkaline Earths 45
21. Titration of Acids 45
22. Pettenkofer's Method of Acidimetry . . . 48
23. Kieffer's Ammonio-Cupric Solution 48
24. Carbonic Acid and Carbonates 50
25. Estimation of Combined Acids in Neutral Salts . . 56
26. Indirect Estimation of Various Substances Alkalimetrically . 58

PART III.

Sect. Page
27. Introduction 61
28. Permanganic Acid and Ferrous Oxide 62
29. Titration of Ferric Salts by Permanganate . . . 66
30. Calculation of Permanganate Analyses . . . 67
31. Chromic Acid and Ferrous Oxide 68
32. Iodine and Hyposulphite 71
33. Analysis of Substances by Distillation with Hydrochloric Acid . 75
34. Arsenious Acid and Iodine 79

PART IV.

35. Introduction 81
36. Chlorine 83
37. Indirect Analyses by Silver and Potassic Chromate . . 85

PART V.

38. Soda Ash, and Commercial Alkaline Products . . 88
39. Potash, Pearlash, and Kainite 94
40. Sulphuric Acid and Sulphates 95
41. Nitric Acid and Nitrates 100
42. Dyad and Triad Iron 115
43. Iron Ores 124
44. Copper 130
45. Zinc 146
46. Manganese 153
47. Nickel 166
48. Cobalt 166
49. Calcium 167
50. Bismuth 168
51. Cadmium 169
52. Tin 169
53. Uranium 171
54. Lead 172
55. Mercury 174
56. Arsenic 178
57. Chromium 180
58. Antimony 182
59. Gold 184
60. Silver 185
61. Iodine 194
62. Chlorine 199
63. Bromine 202
64. Chlorates, Iodates, and Bromates 203
65. Cyanogen 203

Sect. Page
66. Prussiates 206
67. Sulphur 208
68. Sulphuretted Hydrogen 215
69. Phosphoric Acid and Phosphates . . . 217
70. Tannic Acid 233
71. Sugar 237
72. Indigo 242

PART VI.

73. Analysis of Urine 246
74. Analysis of Soils 265
75. Analysis of Manures 272
76. Analysis of Natural Waters and Sewage . . 281
77. Analytical Processes for Water 289
78. Interpretation of Results of Analysis . . . 331
79. Water Analysis without Gas Apparatus . . . 344

PART VII.

80. Volumetric Analysis of Gases . . . 350
81. Gases Estimated Directly and Indirectly . . . 365
82. Hydrochloric, Hydrobromic, and Hydriodic Acids . . 366
83. Analysis of Air and Carbonic Acid . . . 368
84. Indirect Estimations 374
85. Improvements in Gas Apparatus 391
Appendix 414
Tables 419

Names of Elementary Substances of Ordinary Occurrence, with their Symbols and Atomic Weights, as given by the latest and best Authorities.

NAME.	SYMBOL.	ATOMIC WEIGHT.
Aluminium . . .	Al	27·5
Antimony . . .	Sb	122
Arsenic . . .	As	75
Barium . . .	Ba	137
Bismuth . . .	Bi	210
Boron . . .	B	11
Bromine . . .	Br	80
Cadmium . . .	Cd	112
Calcium . . .	Ca	40
Carbon . . .	C	12
Chlorine . . .	Cl	35·5
Chromium . . .	Cr	52·5
Cobalt . . .	Co	58·5
Copper . . .	Cu	63·5
Fluorine . . .	Fl	19
Gold . . .	Au	196·5
Hydrogen . . .	H	1
Iodine . . .	I	127
Iron	Fe	56
Lead . . .	Pb	207
Lithium . . .	Li	7
Magnesium . .	Mg	24
Manganese . . .	Mn	55
Mercury . . .	Hg	200
Molybdenum . . .	Mo	96
Nickel . . .	Ni	58·5
Nitrogen . . .	N	14
Oxygen . . .	O	16
Palladium . . .	Pd	106·5
Phosphorus . .	P	31
Platinum . . .	Pt	197
Potassium . . .	K	39
Silicon	Si	28
Silver . . .	Ag	108
Sodium . . .	Na	23
Strontium . . .	Sr	87·5
Sulphur . . .	S	32
Tin . . .	Sn	118
Uranium . . .	Ur	120
Zinc . . .	Zn	65

Abbreviations and Explanations.

The atomic weights used are based on the latest researches.

The formulæ are constructed on the basis H = 1. O = 16. $H^2O = 18$.

The normal temperature for the preparation and use of standard solutions is 16° C., or about 60° Fahr.

c.c. denotes cubic centimetre.
gm. „ gramme = 15·43235 grains English.
grn. „ grain.
dm. „ decem = 10 fluid grains.
1 Litre = 1000 c.c.
1 c.c. = 1 gm. distilled water at 16° C.
1 dm. = 10 grn. „ „ „

Distilled water is to be used in all the processes, unless otherwise expressed.

Normal Solutions are those which contain one gramme atom of re-agent (taken as monobasic), or an equivalent in some active constituent (*e.g.* oxygen) in the litre.

Decinormal Solutions are one-tenth of that strength = $\frac{N}{10}$.

Centinormal, one-hundredth = $\frac{N}{100}$.

Empirical Standard Solutions are those which contain no exact atomic proportion of re-agent, but are constructed generally so that 1 c.c. = 0·01 gm. (one centigramme) of the substance sought.

A Titrated Solution (from the French word *titre*, title or power) denotes a solution whose strength or chemical power has been accurately found by experiment.

When a chemical substance or solution is directed to be *titrated*, the meaning is that it is to be quantitatively tested for the amount of pure substance it contains by the help of standard or titrated solutions. The term is used in preference to *tested* or *analysed*, because these expressions may relate equally to qualitative and quantitative examinations, whereas titration can only apply to quantitative examination.

ERRATA.

Page 89. Seventeenth line from bottom of page, instead of "§ 39" read "§ 40."
„ 179. Eighth line from top, instead of "standard" read "saturated."
„ 199. Thirteenth line from top, instead of "fig. 32" read "fig. 33."

VOLUMETRIC ANALYSIS

OF

LIQUIDS AND SOLIDS.

PART I.

GENERAL PRINCIPLES.

§ 1. QUANTITATIVE analysis by weight, or gravimetric analysis, consists in separating out the constituents of any compound, either in a pure state or in the form of some new substance of known composition, and accurately weighing the products. Such operations are frequently very complicated, and occupy a long time, besides requiring in many cases elaborate apparatus, and the exercise of much care and experimental knowledge. Volumetric processes, on the other hand, are, as a rule, quickly performed; in most cases are susceptible of extreme accuracy, and need much simpler apparatus. The leading principle of the method consists in submitting the substance to be estimated to certain characteristic reactions, employing for such reactions solutions of known strength, and from the volume of solution necessary for the production of such reaction, determining the weight of the substance to be estimated by aid of the known laws of chemical equivalence.

Volumetric analysis, or quantitative chemical analysis by measure, in the case of liquids and solids, consequently depends upon the following conditions for its successful practice :—

1°. A solution of the re-agent or test, the chemical power of which is accurately known, called the "standard solution."

2°. A graduated vessel from which portions of it may be accurately delivered, called the burette.

3°. The decomposition which the test solution produces with any given substance must be of such a character that its

3

termination is unmistakable to the eye, and thereby the quantity of the substance with which it has combined accurately determined.

Suppose, for instance, that it is desirable to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form chloride of silver, which is insoluble in nitric acid. The proportions in which the combination takes place are 35·5 of chlorine to every 108 of silver; consequently if a standard solution of pure chloride of sodium is prepared by dissolving in water such a weight of the salt as will be equivalent to 35·5 grains of chlorine (= 58·5 grains NaCl) and diluting to the measure of 1000 grains; every single grain measure of this solution will combine with 0·108 grain of pure silver to form chloride of silver, which is precipitated to the bottom of the vessel in which the mixture is made. In the process of adding the salt solution to the silver, drop by drop, a point is at last reached when the precipitate ceases to form. Here the process must stop. On looking carefully at the graduated vessel from which the standard solution has been used, the operator sees at once the number of grain measures which have been necessary to produce the complete decomposition. For example, suppose the quantity used was 520 grain measures; all that is necessary to be done is to multiply 520 by the coefficient for each grain measure, viz. 0·108, which shows the amount of pure silver present to be 56·16 grains.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the estimation by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which have not been described, those will be found in their proper place, but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; besides which, in the majority of instances in which it can be applied, it is equally accurate, and in many cases much more so. For technical purposes, such as the examination of substances used in arts and manufactures, the system has been a great boon, and every day is bringing fresh applications of it both to pure and applied chemical science.

The only condition on which the volumetric system of analysis can be carried on successfully, is that the greatest care is exercised with respect to the graduation of the measuring instruments, and the strength and purity of the standard solutions. A very slight error in the analytical process becomes considerably magnified when calculated for pounds, hundredweights, or tons of the substance tested.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive vegetable colouring matter. The formation of a permanent precipitate, as in the estimation of cyanogen. A precipitate ceasing to form, as in chlorine and silver determinations. The appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by Mohr and others, namely :—

1. Where the determination of the substance is effected by saturation with another substance of opposite properties—generally understood to include acids and alkalies.

2. Where the determination of a substance is effected by a reducing or oxidising agent of known power, including most metals, with their oxides and salts; the principal oxidising agents being potassic permanganate, potassic bichromate, and iodine; and the corresponding reducing agents, ferrous and stannous compounds, and sodic hyposulphite.

3. Where the determination of a substance is effected by precipitating it in some insoluble and definite combination, an example of which occurs in the estimation of silver described above.

This classification does not rigidly include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the reagents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be analysed under two or three heads; copper, for instance, can be determined residually by potassic permanganate; it can also be determined by precipitation with sodic sulphide. The estimation of the same metal by potassic cyanide, on the other hand, would not come under any of the heads.

It will be found, therefore, that liberties have been taken with the arrangement, and for convenient reference all analytical processes applicable to a given body are included under its name.

The application of the process is, of course, limited to the use of such substances as are to be had pure, and whose weight is not variable by exposure; but where even a pure substance of one kind cannot be had as a weight, one of another kind may be used as a substitute, and the required result obtained by calculation. For instance, it is required to ascertain the purity of a specimen of sodic carbonate, and only pure calcic carbonate is at hand to use as a weight, equal weights of the two are taken, and the impure specimen titrated with acid. To arrive at the required answer, it is necessary to find a coefficient or factor by which to convert the number of c.c. required by the sodic carbonate, weighed on the calcic, into that which should be required if weighed on the sodic basis. A consideration of the relative molecular weights of the two bodies will give the factor thus—

$$\frac{\text{Calcic carbonate } 100}{\text{Sodic carbonate } 106} = 0{\cdot}9434.$$

If, therefore, the c.c. found are multiplied by this number, the percentage of pure sodic carbonate will be obtained. The method may be extended to a number of substances, on this principle, with the exercise of a little ingenuity.

VOLUMETRIC ANALYSIS WITHOUT BURETTES OR OTHER GRADUATED INSTRUMENTS.

§ 4. This operation consists in weighing the standard solutions on the balance instead of measuring them. The influence of variation in temperature is, of course, here of no consequence. The chief requisite is a delicate flask, fitted with a tube and blowing ball, as in the burette, fig. 5, or an instrument known as Schuster's alkalimeter may be used. The method is capable of very accurate results, if care be taken in preparing the standard solutions and avoiding any loss in pouring the liquid from the vessel in which it is weighed.

THE BURETTE.

§ 5. This instrument is used for the delivery of an accurately-measured quantity of any particular standard solution. It invariably consists of a long glass tube of even bore, throughout the length of which are engraved, by means of hydrofluoric acid, certain divisions corresponding to a known volume of fluid.

It may be obtained in a great many forms, under the names of their respective inventors, such as Mohr, Gay Lussac, Binks, &c., but as some of these possess a decided superiority over others, it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The burette, with india-rubber tube and clip, contrived by Dr Frederic Mohr, of Bonn, shown in figs. 1 and 2, has the preference above all others for general purposes.

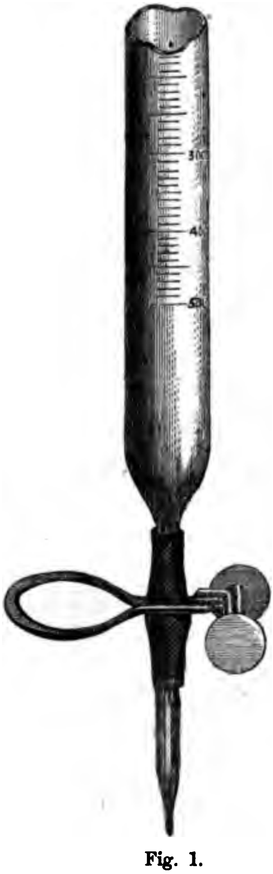

Fig. 1.

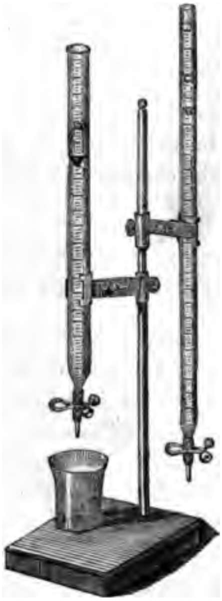

Fig. 2.

The advantages possessed by this instrument are, that its constant upright position enables the operator at once to read off the number of degrees of test solution used for any analysis. The quantity of fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip, and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks' or Gay Lussac's form of instrument. The principal disadvantage, however, of these two latter forms of burette is, that a correct reading can only be obtained by placing them in an upright position, and allowing the fluid to find its perfect level. The preference should therefore, unhesitatingly, be given to Mohr's burette, wherever it can be used; the greatest drawback to it is, that it cannot be used for permanganate in consequence of its india-rubber tube, which decomposes the solution. This, however, can be entirely obviated by the use of the same kind of burette fitted with a delicate glass stop-cock, as shown in fig. 4. This tap burette, if made in a proper

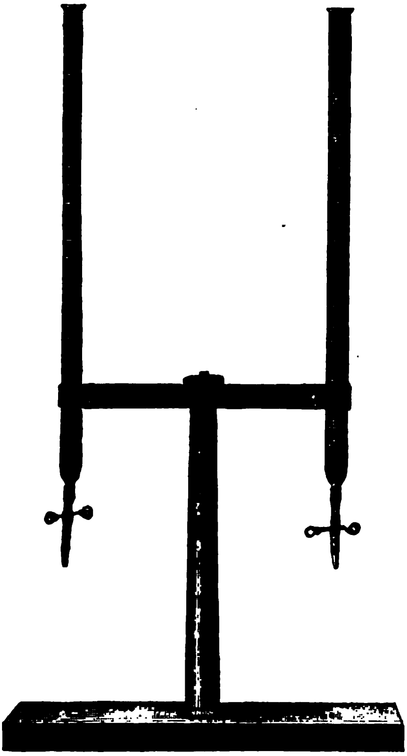
Fig. 3.

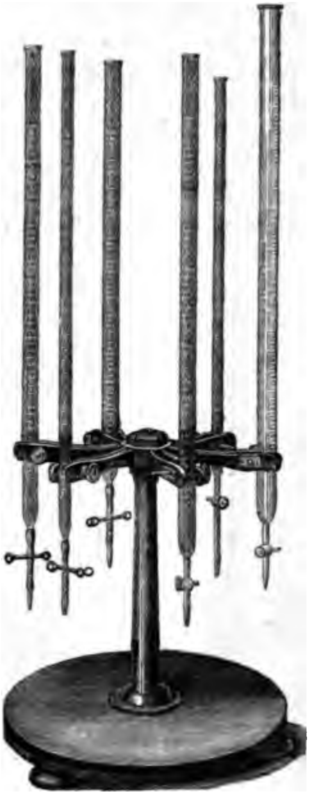
Fig. 4.

manner, is very serviceable, as it can be used not only for permanganate solution, but all others except caustic alkalies, and may also be arranged so as to deliver the solution in drops, leaving both the hands of the operator disengaged. The tap should be ground very accurately, and the end of the plug should have a collar of india-rubber or buckskin fastened on it, so as to prevent the plug from slipping out of its place. Owing to the action of caustic alkalies upon glass, such a burette does not answer well for solutions of potash or soda. Two convenient forms of stand for Mohr's burettes are shown in figs. 3 and 4; in the latter, the arms carrying the burettes revolve.

We are indebted to Mohr for another form of instrument to avoid the contact of permanganate and india-rubber, viz., the foot burette, with elastic ball, shown in fig. 5.

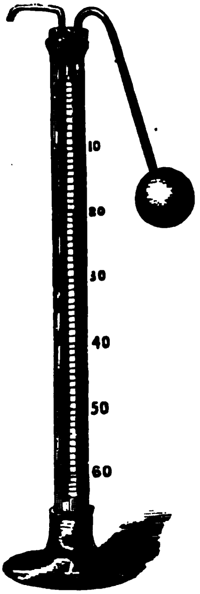

Fig. 5.

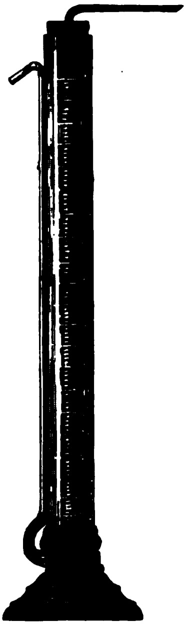

Fig. 6.

The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the ball, which should be large, and have two openings,—one cemented to the tube with marine glue, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills itself with air.

Gay Lussac's burette, supported in a wooden foot, may be used instead of the above form, by inserting a good fitting cork into the open end, through which a small tube bent at right angles is passed. If the burette is held in the right hand, slightly inclined towards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in an horizontal position, to the great danger of spilling the contents, is avoided; at the same time, the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation be more accurately determined.

Fig. 6 will show the arrangement here described.

There is an arrangement of Mohr's burette which is extremely serviceable, when a constant series of analyses of the same character have to be made, such as in alkali works, assay offices, &c. It consists in having a T piece of glass tube inserted between the lower end of the burette and the spring clip, which communicates with a reservoir of the standard solution, placed above, so that the burette may be filled as often as emptied, by a syphon, and in so gradual a manner that no air bubbles occur, as in the case of filling it with a funnel, or pouring in liquid from a bottle; beside which, this plan prevents evaporation or dust in the standard solution

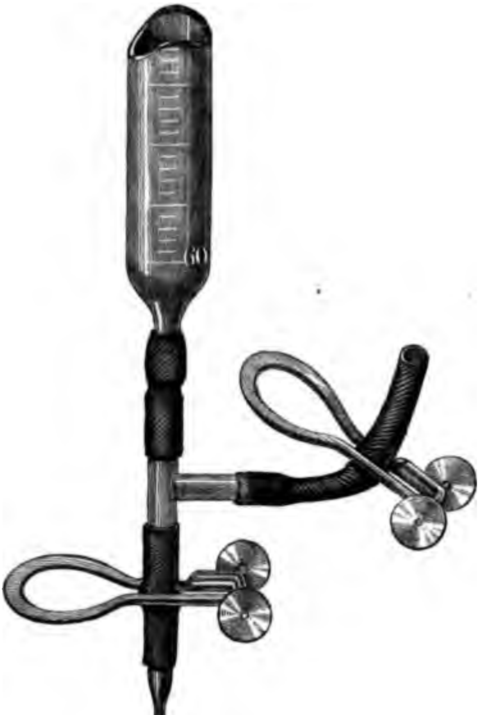

Fig. 7.

either in the burette or reservoir; it is especially applicable to burettes containing caustic alkalies.

Figs. 7 and 8 show the arrangement in detail.

It sometimes happens that a solution requires titration at a hot or even boiling temperature; in which case the ordinary arrangement of Mohr's burette will not be available since the steam rising from the liquid heats the burette and alters the volume of fluid. This may be avoided by using a much longer piece of india-rubber tube, so that the burette stands at the side of the capsule or beaker being heated, and the elastic tube is brought over its edge; the pinch-cock

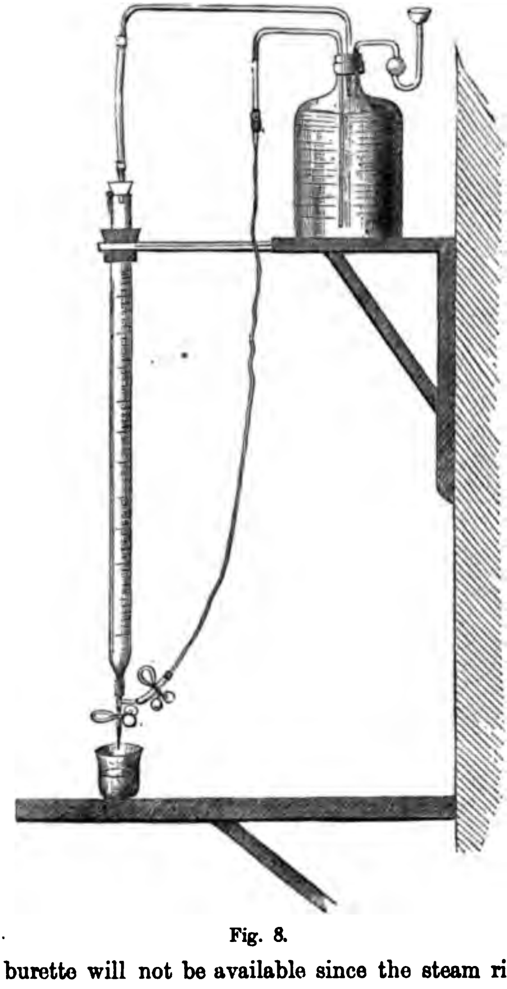

Fig. 8.

is fixed midway; no heat can then reach the body of fluid in the burette, since there can be no conduction past the pinch-cock; if this plan is not adopted, a Gay Lussac or ball burette should be used.

Gay Lussac's burette, shown in fig. 9, should have a wooden support or foot into which it may be inserted, so as to be read correctly. By using it in the following manner, its natural disadvantages may be overcome to a great extent. Having fixed the burette into the foot securely, and filled it, take it up by the foot with the left hand, and resting the upper end upon the edge of the beaker in which the solution to be tested is placed, drop the test fluid from the burette, meanwhile stirring the contents of the beaker with a glass rod held in the right hand; by a slight elevation or depression of the left hand, the flow of test liquid is regulated until the end of the operation is secured, thus avoiding the annoyances which arise from alternately placing the instrument in an upright and horizontal position.

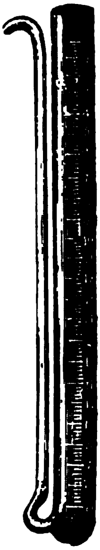

Fig. 9.

Geissler's burette differs from Gay Lussac's in having the fine tube enclosed within the large one, but as it is a difficult instrument to make, it has not found much favour.

Binks', or, as it is sometimes called, the English burette, is well known, and need not be described; it is the least recommendable of all forms.

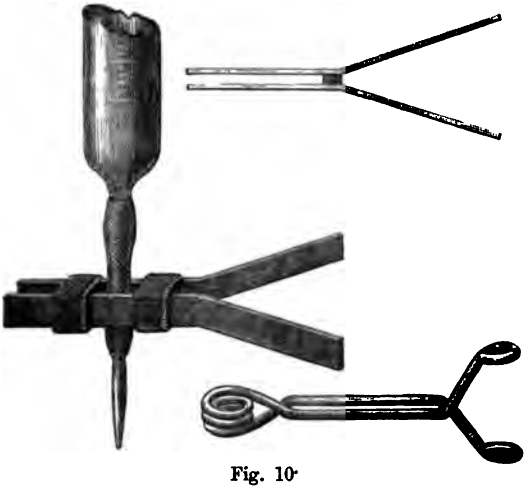

Fig. 10.

It is most convenient to have burettes graduated to contain 25 or 30 c.c. in $\frac{1}{10}$ c.c., 55 or 60 c.c. in $\frac{1}{5}$ c.c., and 100 or 110 c.c. in $\frac{1}{4}$ c.c.

The kind of pinch-cock (quetschhahn) generally used in Mohr's burette is shown in fig. 1. These are made of brass and soldered, which is an objection, as they frequently come to pieces under the action of the solutions. I have for some time used pinch-cocks made of one piece of steel wire, as devised by Hart; the wire is softened by heating and coiling round, as shown in fig. 10.

When the proper shape has been attained the clip is hardened and tempered so as to convert it into a spring.

Another useful pinch-cock is shown in fig. 10. It may be made of hard-wood, horn, or, preferably, of flat glass rod. The levers should be long. A small piece of cork, of the same thickness as the elastic tube of the burette when pressed close, should be fastened at the angles of the levers as shown in the engraving.

The use of any kind of pinch-cock can be avoided, and a very delicate action obtained, by simply inserting a not too tightly fitting piece of solid glass rod into the elastic tube, between the end of the burette and the spit, a firm squeeze being given by the finger and thumb to the elastic tube surrounding the rod, a small canal is opened, and thus the liquid escapes, and of course can be controlled by the operator at his will.

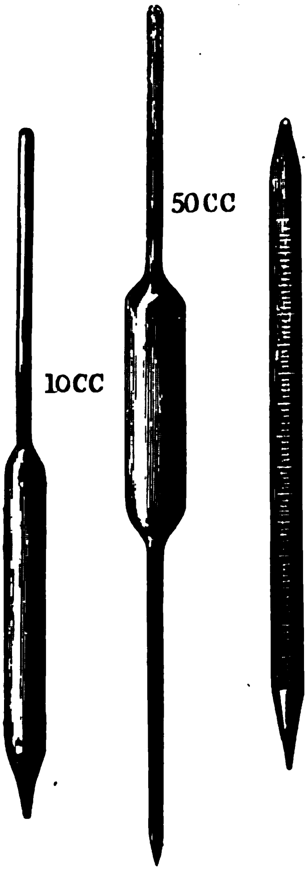

Fig. 11.

THE PIPETTE.

§ 6. The pipettes used in volumetric analysis are of two kinds, viz., those which deliver one certain quantity only, and those which are graduated on the stem, so as to deliver various quantities at the discretion of the analyst. In the former kind, or whole pipette, the graduation may be either that in which the fluid is suffered to run out by its own momentum or in which it is blown out by the breath. The best form is that in which the liquid flows out by its own momentum, but in this case the last few drops empty themselves very slowly, but if the lower end of the pipette be touched against the moistened edge of the beaker or other vessel into which the fluid is poured, the flow is hastened considerably, and in graduating the pipette, it is preferable to do it on this plan.

In both the whole and graduated pipettes, the upper end is narrowed to about ⅛ inch, so that the pressure of the moistened finger is sufficient to arrest the flow at any point.

Fig. 11 shows two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size. It must be borne in mind that the pipette graduated throughout the stem is not a reliable instrument for actual analysis, owing to the difficulty of stopping the flow of liquid at any exact point and reading off the exact measurement. Its chief use is in the approximate estimation of the strength of any standard solution in the course of preparation.

THE MEASURING FLASKS.

§ 7. These indispensable instruments are made of various capacities; they serve to mix up standard solutions to a given volume, and also for the subdivision of the substance to be tested by means of the pipettes, and are in many ways most convenient. They should be tolerably wide at the mouth, and have a well-ground glass stopper, and the graduation line should fall just below the middle of the neck, so as to allow room for shaking up the fluid. Convenient sizes are 100 c.c. (to deliver), 100, 200, 250, 300, 500, and 1000 c.c., the latter all graduated to *contain* the respective quantities. A litre flask is shown in fig. 12.

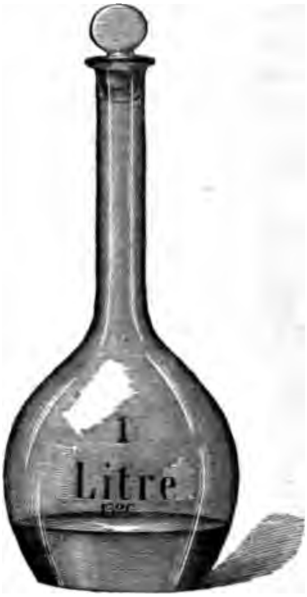

Fig. 12.

ON THE CORRECT READING OF GRADUATED INSTRUMENTS.

§ 8. The surface of liquids contained in narrow tubes is always curved, in consequence of the capillary attraction exerted by the sides of the tube, and consequently there is a difficulty in obtaining a distinct level in the fluid to be measured. If, however, the lowest point of the curve is made to coincide with the graduation mark, a correct proportional reading is always obtained, hence this method of reading is the most satisfactory; see fig. 13. The eye may be assisted materially in reading the divisions on a graduated tube by using a small card, the lower half of which is blackened, the upper remaining white. If the line of division between the black and white be held about an eighth of an inch below the surface of the liquid, and the eye brought on a level with it, the meniscus then can be seen by transmitted light, bounded below by a sharply defined black line. A card of this kind, sliding up and down a support, is of great use in verifying the graduation of the burettes or pipettes with a cathetomer. The burette or pipette is filled with water at the proper temperature, and the contents of each division of 10 c.c. or so carefully read off with the telescope and weighed. In order to do this with pipettes they must be fixed in a burette support, and have over their upper end a tightly fitting elastic tube closed with a pinch-cock. The operator may here consult with advantage the details of graduating and verifying measuring instruments for the analysis of gases as described in Part 7.

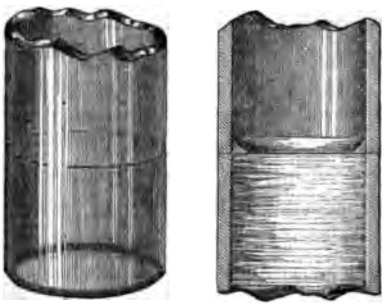

Fig. 13.

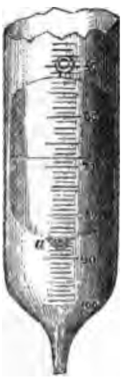

Fig. 14.

Erdmann has contrived a useful little instrument to accompany Mohr's burette, which gives the most accurate reading that can be obtained; its form is shown in fig. 14, and it is known by the name of

Erdmann's float. It consists of an elongated glass bulb, rather smaller in diameter than the burette itself, and weighted at the lower end with a globule of mercury, like an hydrometer. It is drawn to a point at the upper end, and the point is bent round so as to form a small hook, by means of which it can be lifted in and out of the burette with a bent wire; a line is made with a diamond round its middle by means of a lathe, and the coincidence of this line with the graduation mark of the burette is accepted as the true reading. The actual height of the liquid in the burette is not regarded, because if the operator begins with the line on the float, opposite the 0 graduation mark on the burette, the same proportional division is always maintained.

It is essential that the float should move up and down in the burette without wavering, and the circle upon it should always be parallel to the graduations of the burette. One great value of this float is found in testing the accuracy of the burette itself; it enables a strict comparison to be made between say each 10 c.c., with very slight differences in weighing, supposing the instrument to be correct. It is always well, however, to bear in mind that absolute accuracy cannot be obtained in graduating instruments; 5 or 10 milligrammes of water either way in 10 c.c. may safely be disregarded.

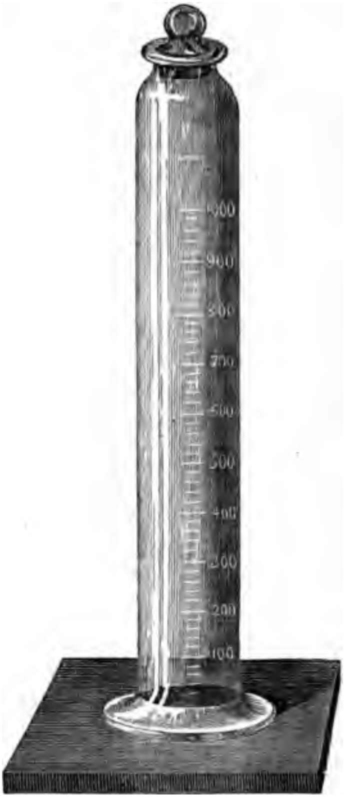

Fig. 15.

To prevent evaporation and the entrance of dust in **Mohr's** burette, the inventor recommends a well polished marble, such as boys play with, to be laid on the open end. A glass bulb on a short stem is preferable, or even a pill box lid, since the marble is liable to tumble over and break any glass apparatus in its fall. In burettes containing caustic alkaline solutions, a cork with carbonic acid tube should be used if the solution is allowed to remain in them for any length of time.

Besides the measuring flasks it is necessary to have graduated vessels of cylindrical form, for the purpose of preparing standard solutions, &c.

Fig. 15 shows a stoppered cylinder for this purpose, generally called a test mixer.

ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE ADOPTED IN VOLUMETRIC ANALYSIS.

§ 9. It is much to be regretted that the decimal system of weights and measures used on the Continent is not universally adopted, for scientific and medicinal purposes, in England. Its great advantage is its uniformity throughout. The unit of weight is the gramme (= 15·43235 grains troy), and a gramme of distilled water at 4° C. or 39° Fahr., measures exactly a cubic centimètre. The kilogramme contains 1000 grammes. The litre 1000 cubic centimètres.

It may not be out of place here to give a short description of the origin of the French decimal system, now used exclusively for scientific purposes in that country, and also in Prussia, Austria, Holland, Sweden, Denmark, Belgium, and Spain.

The commission appointed in France for the purpose of instituting a decimal system of weights and measures, founded their standard on the length of the meridian arc between the pole and equator, the ten-millionth part of which was called the mètre (= 39·3710 English inches), although the accuracy of this measurement has been disputed. It would have been preferable, as since proposed, that the length of a pendulum vibrating exactly 86,400 times in twenty-four hours, or one second for each vibration, equivalent to 39·1372 English inches, should have been taken as the standard mètre, in which case it would have been much easier to verify the standard in case it should be damaged or destroyed. However, the actual mètre in use is equal to 39·371 inches, and from this standard its multiples and subdivisions all proceed decimally, its one-tenth part being the decimètre, one hundredth the centimètre, and one thousandth the millimètre.

In accordance with this, a cube of distilled water at its greatest density, viz., 4° C., or 39° Fahr., whose side measures one decimètre, has exactly the weight of one kilogramme, or 1000 grammes, and occupies the volume of 1 litre, or 1000 cubic centimètres.

This simple relationship between liquids and solids is of great value in a system of volumetric analysis, and even for ordinary analysis by weight; for technical purposes it is equally as applicable as the grain system, the results being invariably tabulated in percentages.

With these brief explanations, therefore, I have only to state that the French decimal system will be mainly used throughout this treatise, but at the same time those who may desire to adhere to the ordinary grain weights, can do so without interfering with the accuracy of the processes described.

As has been before stated, the true cubic centimètre contains one gramme of distilled water at its greatest density, viz., 4° C., or 39° Fahr.; but as this is a degree of temperature which it is impossible to work at for more than a month or two in the year, it is better to take the temperature of 16° C., or about 60° Fahr., as the standard, because in winter most laboratories or rooms have furnaces or other means of warmth, and in summer the same localities would not, under ordinary circumstances, have a much higher degree of heat than 16° C. In order, therefore, that the graduation of instruments on the metrical system may be as uniform as possible with our own fluid measures, the cubic centimètre should contain one gramme of distilled water at 16° C. The true c.c. (*i.e.*, = 1 gm. at 4° C., or 39° Fahr.) contains only 0·999 gm. (strictly 0·998981) at that temperature; but for convenience of working, and for uniformity with our own standards of volume, it is better to make the c.c. contain one gramme at 16° C. The real difference is one thousandth part. The operator, therefore, supposing he desires to graduate his own measuring flasks, must weigh into them 250, 500, or 1000 grammes of distilled water at 16° C., or 60° Fahr.

Fresenius and others have advocated the use of the strict litr by the graduation of instruments, so that the litre shall contain 999 gm. at 16° C. **Mohr**, on the contrary, uses a 1000 gm., at the temperature of 17·5°, the real difference being 1·2 c.c. in the litre, or about one-eight hundredth part.

It will be seen above that I have advocated a middle course on two grounds—1st, That in testing instruments it is much easier to verify them by means of round numbers, such as 5 or 10 gm.;

2nd, That there are many thousands of instruments already in use, varying between the two extremes, and as these cannot well be annihilated, the adoption of a mean will give a less probable amount of error between the respective instruments; and, moreover, the difference between the litre at 4° and 16° being one-thousandth part, it is easy to correct the measurement for the exact litre.

It matters not which plan is followed, if all the instruments in a particular set coincide with each other; but it would be manifestly wrong to use one of Mohr's burettes with one of Fresenius' measuring flasks. Operators can, however, without much difficulty, re-mark their measuring flasks to agree with their smaller graduated instruments, if they are found to differ to any material extent.

In the preparation of standard solutions, one thing must especially be borne in mind, namely, that saline substances on being dissolved in water have a considerable effect upon the volume of the resulting liquid. The same is also the case in mixing solutions of various salts or acids with each other. (See Gerlach, "Specifische Gewichte der Salzlösungen;" also Gerlach, "Sp. Gewichte von wassrigen Lösungen," Zeitschrift für An. Chem., vol. viii. p. 245.)

In the case of strong solutions, the condensation in volume is as a rule considerable; and, therefore, in preparing such solutions for volumetric analysis, or in diluting such solutions to a given volume for the purpose of removing aliquot portions subsequently for examination, sufficient time must be given for liquids to assume their constant volume at the standard temperature. If the strength of a standard solution is known for one temperature, the strength corresponding to another temperature can only be calculated if the rate of expansion by heat of the liquid is known. The variation cannot be estimated by the known rule of expansion in distilled water; for Gerlach has shown that even weak solutions of acids and salts expand far more than water for certain increments of temperature. The rate of expansion for pure water is known, and may be used for the purpose of verifying the graduation of instruments, where extreme accuracy is required. The following short table furnishes the data for correction. (See also Dittmar, "Watt's Chem. Dict.," Vol. I, p. 256.)

The weight of 1000 c.c. of water of t° C., when determined by means of brass weights in air of t° C., and at 0·76 m.m., pressure is equal to 1000 – x gm.

Slight variations of atmospheric pressure may be entirely disregarded.

t°	10	11	12	13	14	15	16	17	18	19	
x	1·34	1·43	1·52	1·63	1·76	1·89	2·04	2·2	2·37	2·55	
t°	20	21	22	23	24	25	26	27	28	29	30
x	2·74	2·95	3·17	3·39	3·63	3·88	4·13	4·39	4·67	4·94	5·24

Bearing the foregoing remarks in mind, therefore, the safest plan in the operations of volumetric analysis, so far as measurement is concerned, is to use solutions as dilute as possible. Absolute accuracy in estimating the strength of standard solutions can only be secured by weight, the ratio of the weight of the solution to the weight of active substance in it being independent of temperature.

The accurate graduation of burettes and pipettes can only be done by carefully constructed machines, and is, therefore, generally speaking, beyond the compass of the analyst himself; nevertheless, they should be carefully tested by him before being used, as, unfortunately, they do not always possess the accuracy to which they pretend. In the verification of both burettes and pipettes, it is only necessary to allow ten cubic centimètres of distilled water to flow from the instrument to be tested into a dry and accurately tared flask or beaker. If the weight at 16° C., or 60° Fahr., is 10 grammes, it is sufficient; the next ten c.c. may be tried in like manner, and so on until the entire capacity is proved; differences of 5 or 10 milligrammes may be disregarded.

Beside the litre flask, it is advisable to have flasks graduated for 100, 200, 250, 300, and 500 c.c., as they are extremely serviceable in dividing small quantities of substance into still smaller proportional parts. Suppose for instance, it is desired to take the tenth part of a solution for the purpose of separating any single constituent, let it be put into a 200 c.c. flask, which is then filled to the mark with water or other appropriate liquid, and well shaken; 20 c.c. taken out with a pipette will at once give the quantity required.

Burettes, pipettes, and flasks may also be graduated in grains, in which case it is best to take 10,000 grains as the standard of measurement. In order to lessen the number of figures used in the grain system, so far as liquid measures are concerned, I propose that ten fluid grains be called a decem, or for shortness dm.; this term corresponds to the cubic centimètre bearing the same proportion to the 10,000 grain measure as the cubic centimètre does to the litre, namely, the one-thousandth part. The use of a term like this will serve to prevent the number of figures, which are unavoidably introduced, by a small unit like the grain.

Its utility is principally apparent in the analysis for percentages, particulars of which will be found hereafter.

The 1000 grain burette or pipette will, therefore, contain 100 decems, the 10,000 gr. measure, 1000 dm., and so on.

The capacities of the various instruments graduated on the grain system may be as follows:—

Flasks: 10000, 5000, 2500, and 1000 grs., = 1000, 500, 250, and 100 dm. Burettes: 300 grs. in 1 gr. divisions, for very delicate purposes = 30 dm. in $\frac{1}{10}$; 600 grs. in 2-gr. divisions, or $\frac{1}{5}$ dm.; 1100 grs. in 5-gr. divisions, or $\frac{1}{2}$ dm.; 1100 grs. in 10-gr. divisions, or 1 dm. The burettes are graduated above the 500 or 1000 grs. in order to allow of analysis for percentages by the residual method. Whole pipettes to deliver 10, 20, 50, 100, 200, 500 and 1000 grs.; graduated ditto, 100 gr. in $\frac{1}{10}$ dm.; 500 grs. in $\frac{1}{2}$ dm.; 1000 grs. in 1 dm.

Those who may desire to use the decimal systems constructed on the gallon measure = 70,000 grains, will bear in mind that the "septem" of Mr. Griffin, or the "decimillen" of Mr. Acland, are each equal to 7 grs., and therefore bear the same relation to the pound = 7000 grs., as the cubic centimètre does to the litre, or the decem to the 10,000 grs. An entirely different set of tables for calculations, &c., is required for these systems, but the analyst may readily construct them when once the principles contained in this treatise are understood.

VOLUMETRIC ANALYSIS BASED ON THE SYSTEM OF CHEMICAL EQUIVALENCE AND THE PREPARATION OF NORMAL TITRATED SOLUTIONS.

§ 10. When analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special re-agent, and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry a distinct standard acid was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions.

Griffin and Ure appear to have been the first to suggest the use of standard test solutions based on the atomic system, and following in their steps, Mohr has worked out and verified many methods of analysis, which are of great value to all who concern themselves with scientific and especially technical chemistry. Not only has Mohr done this, but in addition to it, he has enriched his processes with so many original investigations, and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

His "Lehrbuch der Chemisch-Analytischen Titrirmethode," is the most complete treatise on the subject, and well deserving the thanks of all students of the science.

But to return to the explanation of the system. Normal solutions as a general rule are prepared so that one litre at 16° C. shall contain the hydrogen equivalent of the active reagent weighed in grammes (H = 1).

Decinormal solutions are made one-tenth, and centinormal one-hundredth of this strength, and may be shortly designated as $\frac{N}{10}$ and $\frac{N}{100}$ solutions.

In the case of univalent substances such as silver, iodine, hydrochloric acid, sodium, &c., the equivalent and the atomic (or in the case of salts, molecular) weights are identical; thus a normal solution of hydrochloric acid must contain 36·5 grammes of the acid in a litre of fluid, and sodic hydrate 40 grammes. In the case of bivalent substances such as lead, calcium, oxalic acid, sulphurous acid, carbonates, &c., the equivalent is one-half of the atomic (or in the case of salts, molecular) weight; thus a normal solution of oxalic acid would be made by dissolving 63 grammes of the crystallized acid in distilled water, and diluting the liquid to the measure of one litre.

Further, in the case of trivalent substances such as phosphoric acid, a normal solution of sodic phosphate would be made by weighing $\frac{358}{3} = 119{\cdot}3$ grammes of the salt dissolved in distilled water, and diluting to the measure of one litre.

One important point, however, must not be lost sight of, namely, that in preparing solutions for volumetric analysis the value of a reagent as expressed by its equivalent hydrogen-weight must not always be regarded, but rather its particular reaction in any given analysis; for instance, tin is a quadrivalent metal, but when using stannous chloride as a reducing agent in the analysis of iron, the half, and not *the fourth* of its molecular weight is required, as is shown by the equation $Fe^2\,Cl^6 + Sn\ Cl^2 = 2\ Fe\ Cl^2 + Sn\ Cl^4$.

In the same manner with a solution of potassic permanganate $Mn\ KO^4$ when used as an oxidising agent, it is the available oxygen which has to be taken into account, and hence in constructing a normal solution one-fifth of its molecular weight $\frac{158}{5} = 31{\cdot}6$ grammes must be contained in the litre.

Other instances of a like kind occur, the details of which will be given in the proper place.

A further illustration may be given in order to show the method of calculating the result of this kind of analysis.

Each c.c. of $\frac{N}{10}$ silver solution will contain $\frac{1}{10000}$ of the atomic weight of silver = 0·0108 gm., and will exactly precipitate $\frac{1}{10000}$ of the atomic weight of chlorine = 0·00355 gm. from any solution of a chloride.

In the case of normal oxalic acid each c.c. will contain $\frac{1}{2000}$ of the molecular weight of the acid = 0·063 gm., and will neutralize $\frac{1}{2000}$ of the molecular weight of sodic monocarbonate = 0·053 gm., or will combine with $\frac{1}{2000}$ of the atomic weight of a dyad metal such as lead = 0·1035 gm., or will exactly saturate $\frac{1}{1000}$ of the molecular weight of sodic hydrate = 0·040 gm., and so on.

Where the 1000 grain measure is used as the standard in place of the litre, 63 grains of oxalic acid would be used for the normal solution; but as 1000 grains is too small a quantity to make, it is better to weigh 630 grains, and make up the solution to 10,000 grain measures = 1000 dm. The solution would then have exactly the same strength as if prepared on the litre system, as it is proportionally the same in chemical power; and either solution may be used indiscriminately for instruments graduated on either scale, bearing in mind that the substance to be tested with a c.c. burette must be weighed on the gramme system, and *vice versâ*, unless it be desired to calculate one system of weights into the other.

The great convenience of this equivalent system is, that the numbers used as coefficients for calculation in any analysis are familiar, and the solutions agree with each other, volume for volume. We have hitherto, however, looked only at one side of its advantages. For technical purposes, the plan allows the use of all solutions of systematic strength, and simply varies the amount of substance tested according to its equivalent weight.

Thus, the normal solutions say, are—

Crystallised oxalic acid = 63 gm. per litre.
Sulphuric acid = 49 gm. „
Hydrochloric acid = 36·5 gm. „
Nitric acid = 63 gm. „
Anhydrous sodic carbonate = 53 gm. „
Sodic hydrate = 40 gm. „
Ammonia = 17 gm. „

100 c.c. of any one of these normal acids should exactly neutralise 100 c.c. of any of the normal alkalies, or the corresponding amount of pure substance which the 100 c.c. contain. In commerce we continually meet with substances used in manufactures which are not pure. It is necessary to know how much pure substance they contain.

Let us take, for instance, refined soda ash (sodic carbonate). If it were absolutely pure, 5·3 gm. of it should require exactly 100 c.c. of any normal acid to saturate it. If we therefore weigh that quantity, bring it into solution with water, add litmus, and deliver into the mixture the normal acid from a 100 c.c. burette; the number of c.c. required to saturate it will show the percentage of pure sodic carbonate in the sample. Suppose 90 c.c. are required = 90 %.

Again—a manufacturer buys common oil of vitriol, and requires to know the exact percentage of pure hydrated acid in it; 4·9 gm. is weighed, diluted with water, litmus added, and normal alkali delivered in from a 100 c.c. burette till saturated; the number of c.c. used will be the percentage of real acid. Suppose 58·5 o.c. are required = 58·5 %.

On the grain system, in the same way, 53 grains of the sample of soda ash would require 90 dm. of normal acid, also equal to 90 %.

Or, suppose the analyst desires to know the equivalent percentage of dry caustic soda, free and combined, contained in the above sample of soda ash, without calculating it from the carbonate found as above, 3·1 gm. is treated as before, and the number of c.c. required is the percentage of sodic oxide. In the same sample 52·6 c.c. would be required = 52·6 per cent. of sodic oxide, or 90 per cent. carbonate.

The rules, therefore, for obtaining the percentage of pure substance in any commercial article, such as alkalies, acids, and various salts, by means of systematic normal solutions such as have been described, are these—

1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ of the molecular weight in

grammes of the substance to be analyzed is to be weighed for titration (according to its atomicity), and the number of c.c. required to produce the desired reaction is the percentage of the substance whose atomic weight has been used:

With decinormal solutions $\frac{1}{100}$ or $\frac{1}{200}$ of the molecular weight in grammes is taken, and the number of c.c. required will, in like manner, give the percentage.

Where the grain system is used it will be necessary, in the case of titrating with a normal solution, to weigh the whole or half the molecular weight of the substance in grains, and the number of decems required will be the percentage.

With decinormal solutions $\frac{1}{10}$ or $\frac{1}{20}$ of the molecular weight in grains is taken, and the number of decems will be the percentage.

It now only remains to say, with respect to the system of weights and measures to be used, that the analyst is at liberty to choose his own plan. Both systems are susceptible of equal accuracy, and he must study his own convenience as to which he will adopt.

The normal solutions prepared on the gramme system are equally applicable for that of the grain, and *vice versâ*, so that there is no necessity for having distinct solutions for each system. It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know, a weighed or measured quantity of it is brought under the acid burette and saturated exactly by the aid of litmus, 32 c.c. being required. The calculation is as follows:—

The molecular weight of potassic hydrate being 56, 100 c.c. of normal acid will saturate 5·6 gm.; therefore, as 100 c.c. are to 5·6 gm., so are 32 c.c. to x, $\frac{5{\cdot}60 \times 32}{100} = 1{\cdot}792$ KHO.

The simplest way, therefore, to proceed, is to multiply the number of c.c. of test solution required in any analysis, by the $\frac{1}{1000}$ (or $\frac{1}{2000}$ if bivalent) of the molecular weight of the substance sought, which gives at once the amount of substance present.

An example may be given—1 gm. of marble or limestone is taken for the estimation of pure calcic carbonate, and exactly saturated with standard nitric or hydrochloric acid—(sulphuric or oxalic acid are, of course, not admissible) 17·5 c.c. were required, therefore, 17·5 × ·050 (the $\frac{1}{2000}$ of the molecular weight of $CaCO^3$) give

0·875 gm., and as 1 gm. of substance only was taken=87·5 % calcic carbonate.

In some cases it is advisable to have standard solutions based on an empirical instead of an atomic system, in which case each solution only suffices for the estimation of one special substance. This is the case in the analysis of urine and a few other substances, particulars of which will be found in their proper places.

There are other test solutions which, in consequence of their proneness to decomposition, cannot be kept at any particular strength for a length of time, consequently they must be titrated on every occasion before being used. Stannous chloride and sulphurous acid are examples of such solutions. Special vessels have been devised for keeping solutions liable to alter in strength by access of air, as shown in figs. 16 and 17.

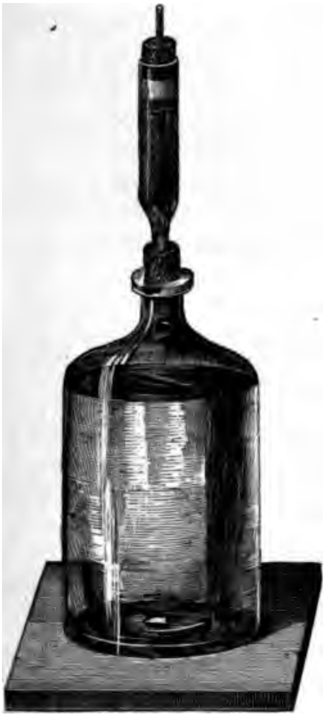
Fig. 17.

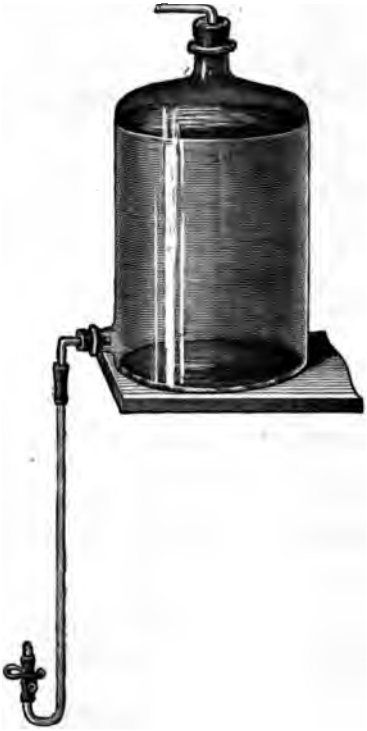
Fig. 16.

Fig. 16 was designed by **Graham**, and is especially applicable to caustic alkaline solutions, the tube passing through the cork being filled with a mixture of Glauber's salt and quicklime, previously dried and gently ignited.

Fig. 17, designed by Mohr, is a considerable improvement upon this, since it allows of the burette being filled with the solution from the store bottle quietly, and without any access of air whatever. The vessel can be used for caustic alkalies, stannous chloride, permanganate, sulphurous acid, or any other liquid liable to undergo change by absorbing oxygen. The corks are dried and soaked in melted paraffine, and a thin layer of petroleum oil, such as is used for burning, is poured on the top of the solution, where, of course, owing to its low specific gravity, it always floats, placing an impermeable division between the air and the solution; and as this body (which should always be as pure as possible) is not affected by these reagents in their dilute state, this form offers great advantages. Solutions not affected chemically by contact with air should nevertheless be kept in bottles, the corks or stoppers of which are perfectly closed, and tied over with india-rubber or bladder to prevent evaporation, and should further be always shaken before use, in case they are not quite full.

ON THE DIRECT AND INDIRECT PROCESSES OF ANALYSIS AND THEIR TERMINATION.

§ 11. The direct method includes all those analyses where the substance under examination is decomposed by simple contact with a known quantity or equivalent proportion of some other body capable of combining with it, and where the end of the decomposition is manifested in the solution itself.

It also properly includes those analyses in which the substance reacts upon another body to the expulsion of a representative equivalent of the latter, which is then estimated as a substitute for the thing required.

Examples of the first kind are readily found in the process for the determination of iron by potassic permanganate, where the beautiful rose colour of the permanganate asserts itself as the end of the reaction.

The testing of acids and alkalies comes, also, under this class, the great sensitiveness of litmus or turmeric allowing the most trifling excess of acid or alkali to alter its colour.

The second is exemplified in the analysis of manganese ores, and also other peroxides and oxygen acids, by boiling with hydrochloric acid. The chlorine evolved is estimated as the equivalent of the quantity of oxygen which has displaced it. We are indebted to Bunsen for a most accurate and valuable series of processes based on this principle.

The indirect or residual method is such that the substance to be analysed is not estimated itself, but the excess of some other body added for the purpose of combining with it or of decomposing it, and the quantity or strength of the body added being known, and the conditions under which it enters into combination being also known, by deducting the remainder or excess (which exists free) from the original quantity, it gives at once the proportional quantity of the substance sought.

An example will make the principle obvious:—Suppose that a sample of native calcic or baric carbonate is to be tested. It is not possible to estimate it with standard nitric or hydrochloric acid in the exact quantity it requires for decomposition. There must be an excess of acid and heat applied also to get it into solution; if, therefore, a known excessive quantity of standard acid be first added, and solution obtained, and the liquid then titrated backward with litmus and standard alkali, the quantity of free acid can be exactly determined, and consequently that which is combined also.

In some analyses it is necessary to add a substance which shall be an indicator of the end of the process; such for instance, is litmus in alkalimetry, potassic chromate in silver and chlorine, and starch in iodine, estimations.

There are other processes, the end of which can only be determined by an indicator separate from the solution; such is the case in the estimation of iron by potassic bichromate, where a drop of the liquid is brought into contact with another drop of solution of red potassic prussiate on a white slab or plate; when a blue colour ceases to form by contact of the two liquids, the end of the process is reached.

The latter is somewhat less reliable, in point of delicacy, than the others, but nevertheless, with care and practice, is susceptible in most cases of very tolerable accuracy.

PART II.

ANALYSIS BY SATURATION.

ALKALIMETRY AND ACIDIMETRY.

§ 12. GAY LUSSAC based his system of alkalimetry upon a titrated solution of sodic carbonate, with a corresponding solution of sulphuric acid, and as this was devised mainly for the use of soda manufacturers it was doubtless the best system for that purpose. It possesses the recommendation that a pure standard solution of sodic carbonate can be more readily obtained than any other form of alkali. Mohr has introduced the use of caustic alkali instead of a carbonate, the strength of which is established by a standard solution of oxalic or sulphuric acid. The principal advantage in the latter system is, that in testing the strength of acids with a caustic alkali, the well-known interference produced by carbonic acid is avoided. The caustic solutions of soda, potash, or ammonia should be kept in bottles like those shown in Figs. 16 and 17, so as to prevent their absorbing carbonic acid.

INDICATORS USED IN ALKALIMETRY.

1. Litmus Solution.

§ 13. In testing both acids and alkalies it is customary to employ a solution of litmus as indicator, which may be prepared by taking about 10 grammes of the solid material, and digesting it with half a litre of distilled water for a few hours in a warm place, decanting the clear liquid from the sediment, adding a few drops of dilute nitric acid so as to produce a violet colour, and preserving it in an open bottle with narrow neck and bulb tube for removing drops as may be required—fig. 18.

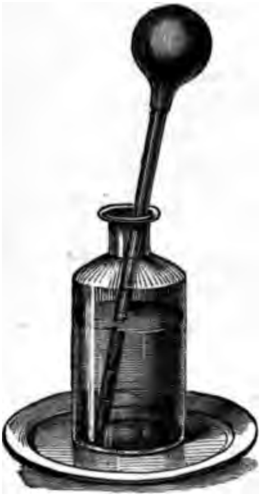
Fig. 18.

If at any time the colour of the liquid.

should partially disappear, it may be restored again by exposing it to the air in an open dish.

A purer solution of litmus may be prepared as follows:—Boil the litmus, previously reduced to coarse powder, two or three times with alcohol of about 80 per cent., and throw the liquid so obtained away (this treatment removes some colouring matter which is a hindrance to the proper reaction), then digest the litmus repeatedly with cold distilled water till all soluble colour is extracted, let the mixed washings settle clear, decant and add to them a few drops of concentrated sulphuric acid until quite red, then heat to boiling, this will decompose the alkaline carbonates and convert them into sulphates, now cautiously add baryta water until the colour is restored to blue or violet, let the baric sulphate settle perfectly and decant into a proper vessel for use.

Litmus, prepared and kept in this way, is very sensitive to dilute acids and alkalies; with the slightest excess of oxalic, sulphuric, hydrochloric, or nitric acids it gives a pink red, and with caustic soda or potash, a blue colour; with ammonia or the bicarbonated alkalies it retains its violet colour, and the same with most of the neutral salts of the weak acids, such as sodic or ammonic acetate or borax.

Free carbonic acid interferes considerably with the production of the blue colour, and its interference in titrating acid solutions with alkaline carbonates can only be got rid of by boiling the liquid during the operation, in order to displace the gas from the solution. If this is not done, it is easy to overstep the exact point of neutrality in endeavouring to produce the blue colour; the same difficulty is also found in obtaining the pink red when acids are used for titrating alkaline carbonates, hence the great value of the caustic alkaline solutions free from carbonic acid in acidimetry.

Litmus paper is simply made by dipping strips of filtering paper in the solution and drying them; if required red, the liquid is slightly acidified.

It sometimes occurs that testing by litmus is required at night; ordinary gas or lamp light is not adapted for showing the reaction in a satisfactory manner, but a very sharp line of demarcation between red and blue may be found in using a monochromatic light; with the yellow sodium flame, the red colour appears perfectly colourless, while the blue or violet appears like a mixture of black ink and water, the transition is very sudden and even sharper than the change by daylight.

The operation should be conducted in a perfectly dark room,

PREPARATION OF THE NORMAL ACID AND ALKALINE SOLUTIONS.

1. Normal Sodic Carbonate

= 53 gm. Na^2CO^3 per litre.

§ 14. This solution is made by dissolving 53 gm. of pure and dry sodic monocarbonate in distilled water, and diluting to 1 litre at 16° C. If the salt is not at hand, the solution may be made as follows :—

About 85 gm. of pure sodic bicarbonate is heated to dull redness, not to fusion, in a platinum, silver, or porcelain crucible, for fully ten minutes, to expel the carbonic acid, then placed under an exsiccator to cool; when placed upon the balance it will be found that very little more than 53 gm. remain. The excess is removed as quickly as possible, and the contents of the crucible washed into a beaker, and as soon as the salt is dissolved the solution is decanted into a litre flask and filled up to the mark with distilled water, at 16° C.

2. Normal Sulphuric Acid

= 49 gm. H^2SO^4 per litre.

About 30 c.c. of pure sulphuric acid of sp. gr. 1·840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to the litre. The solution must now be tested by the normal alkali, which is best done by putting 10 c.c. of the latter into a small beaker or flask with litmus, and allowing the acid to flow from a 10 or 12 c.c. pipette, divided into $\frac{1}{10}$ c.c., until the point of neutrality is reached. If more than 10 c.c. are required the acid is too weak; if less, too strong. If the acid from which the solution was made was of the sp. gr. mentioned, it will generally be too strong, which is preferable. Suppose, therefore, it required 8·9 c.c. to saturate the 10 c.c. of alkali, 890 c.c. will be required to make one litre of standard acid; remove, therefore, the excess from the cylinder and dilute to exactly one litre. Now, test again with the pipette, if the previous examination was correct, 10 c.c. of each solution should exactly neutralise each other. As a further check upon the accurate strength of the solution it is advisable to use larger quantities, say 50 or 100 c.c. for the final adjustment.

The solution may also be controlled by precipitation with baric chloride, in which case 10 c.c. should produce as much baric sulphate as is equal to 0·49 gm. of sulphuric acid, or 49 gm. per. litre.

3. Normal Oxalic Acid.

= 63 gm. $C^2O^4H^2$, $2H^2O$ per litre.

This solution possesses the advantage that it may be established directly, by weighing 63 gm. of the pure crystallised acid in a litre of water.

The acid should be re-crystallised repeatedly, thoroughly air dried, but not in the slightest degree effloresced. The solution is apt to deposit some of the acid at low temperatures, but otherwise keeps well, and will bear heating without volatilising the acid.

4. Normal Hydrochloric Acid

= 36·5 gm. HCl per litre.

It has been shown by Roscoe and Dittmar (Chem. Soc. Q. J. vol. 12) that a solution of hydrochloric acid containing 20·2 per cent. of the gas when boiled at about 760 m.m. pressure, loses acid and water in the same proportion, and the residue will therefore have the constant composition of 20·2°/₀ or a specific gravity of 1·10 About 181 gm. of liquid acid of this gravity, diluted to 1 litre, serves very well to form an approximate normal acid.

The actual strength may be determined by $\frac{N}{10}$ silver solution, or by titration with an exactly weighed quantity of pure sodic monocarbonate. Hydrochloric acid is useful on account of its forming soluble compounds with the alkaline earths, but it has the disadvantage of volatilising at a boiling heat. Dittmar says that this may be prevented by adding a few grammes of sodic sulphate; in many cases this would be inadmissible, for the same reason that sulphuric acid cannot be used. Standard hydrochloric acid is chiefly valuable as a check to alkaline solutions, inasmuch as, owing to the great delicacy of the reaction between chlorine and silver, the strength of a solution of the acid may be exactly found, and it thus serves more especially as a standard for the caustic alkaline solutions.

5. Normal Nitric Acid

= 63 gm. HNO^3 per litre.

In order to obtain a rigidly exact normal acid, it is advisable to graduate it by pure calcic carbonate, either in the form of the purest Iceland spar, as recommended by Pincus, or by artificial carbonate, prepared with great care by precipitating pure calcic chloride with ammonic carbonate, and boiling the resulting precipitate until it becomes dense; it is then washed thoroughly with hot water, dried, ignited gently, and preserved in bottles closed with a chloride of calcium tube.

By means of either of these forms of calcic carbonate, it is possible at any time to titrate a dilute nitric acid, so as to bring it to the normal state, but as more acid must be used for the decomposition than is actually required to saturate the lime and expel the carbonic acid, the excess must be estimated by the help of normal alkali.

It is a question whether this method is more exact in its results than by titrating the nitric acid direct by means of sodic carbonate. If the very purest sodic carbonate is used, and every precaution taken in igniting and weighing it, there cannot be much scope for error; nevertheless, it is desirable to check the results in every possible way, and as pure calcic carbonate is not difficult to obtain, and does not contract moisture like sodic carbonate, it is a reliable basis upon which to work.

The nitric acid used should be colourless, free from chlorine and nitrous acid, sp. gr. from 1·35 to 1·4. If coloured from the presence of nitrous or hyponitrous acids, it should be mixed with two volumes of water, and boiled until white. When cold it may be diluted and titrated as above. 1 gm. of pure Iceland spar in small pieces should require 20 c.c. of acid, supposing it to be rigidly normal; if slightly stronger or weaker, the exact difference must be found, so that a constant factor may be obtained by which to bring it by calculation to the normal state.

Lime, baryta, and strontia, in the caustic state, or combined with carbonic acid, are dissolved by the aid of heat in an excess of normal acid, and then titrated with normal alkali. Chlorides and nitrates of the same bases are precipitated hot with ammonic carbonate containing caustic ammonia, thoroughly washed on a filter, with hot water, and both filter and precipitate, while still moist, pushed through the funnel into a flask, and titrated as above; by deducting the number of c.c. of alkali from the original quantity of acid used, the proportion of pure base, or its compounds, may be obtained.

6. Normal Caustic Alkali

= 40 gm. NaHO, 56 gm. KHO, or 17 gm. NH^3 per litre.

May consist of either soda, potash, or (less recommendably) ammonia. The two first are prepared from pure carbonates by the aid of freshly burnt lime as follows :—

Two parts of pure sodic or potassic carbonate are to be dissolved in 20 parts of distilled water and boiled in a clean iron pot; during the boiling one part of fresh quick-lime, made into a cream with water, is to be added little by little, and the whole boiled until all the carbonic acid is removed, which may be known by the clear solution producing no effervescence on the addition of dilute acid; the vessel is covered closely, and set aside to cool and settle; when cold, the clear supernatant liquid should be poured or drawn off and titrated by normal acid, and made of the proper strength as directed for sulphuric acid.

The trouble of making the soda solution by means of lime may be avoided with advantage by using the pure sodic hydrate manufactured from metallic sodium. It may be obtained perfectly pure and free from carbonic acid. About 42 gm. is dissolved in 800 c.c. of water, titrated with normal acid, and diluted so that it corresponds with the acid, volume for volume.

Normal caustic ammonia is simply made by diluting the strong and freshly made commercial solution, so that volume for volume it corresponds with normal acid.

In preparing any of these three alkaline solutions, they should be exposed as little as possible to the air, and when the strength is finally settled, should be preserved in one of the bottles shown in fig. 16 or 17.

ESTIMATION OF THE CORRECT STRENGTH OF STANDARD SOLUTIONS NOT STRICTLY NORMAL OR SYSTEMATIC.

§ 15. In discussing the preparation of the foregoing standard solutions, it has been assumed that they shall be strictly and absolutely correct,—that is to say, if the same litre measure be filled first with any alkaline solution, then with an acid solution, and the two mixed together, a perfectly neutral solution shall result, so that a drop or two either way will upset the equilibrium.

Where it is possible to weigh directly a pure dry substance, this approximation may be very closely reached. Sodic monocarbonate, for instance, admits of being thus accurately weighed, and so also does oxalic acid. On the other hand, the caustic alkalies cannot be so weighed, nor can the liquid acids. An approximate quantity, therefore, of these substances must be taken, and the exact power of the solution found by experiment.

In titrating such solutions it is exceedingly difficult to make them so exact in strength that the precise quantity, to a drop or two, shall neutralise each other. In technical matters a near approximation may be sufficient, but in scientific investigations it is of the greatest importance that the utmost accuracy should be obtained; it is, therefore, advisable to ascertain the actual difference, and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a standard sulphuric acid is prepared which does not rigidly agree with the normal sodic carbonate, not at all an uncommon occurrence, as it is exceedingly difficult to hit the precise point; in order to find out the exact difference, about 3 gm. of absolutely pure sodic bicarbonate is to be ignited in platinum crucible until converted into monocarbonate, then placed under the exsiccator and allowed to cool; when placed on the balance, suppose the weight found to be 1·9 gm., it is then dissolved and titrated with the standard acid, of which 36·1 c.c. are required to reach the exact neutral point.

If the acid were rigidly exact it should require 35·85 c.c.; in order, therefore, to find the factor necessary to bring the quantity of acid used in the analysis to an equivalent quantity of normal strength, the number of c.c. actually used must be taken as the denominator and the number which should have been used had the acid been strictly normal, as the numerator, thus:—

$$\frac{35{\cdot}85}{36{\cdot}1} = 0{\cdot}993\,;$$

0·993 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid used in any analysis in order to reduce it to normal strength, and should be marked upon the bottle in which it is kept.

On the other hand, suppose that the acid is too strong, and that 35·2 c.c. were required instead of 35·85,

$$\frac{35{\cdot}85}{35{\cdot}2} = 1{\cdot}0184\,;$$

1·0184 is therefore the factor by which it is necessary to multiply the number of c.c. of that particular acid in order to bring it to the normal strength.

It is, of course, taken for granted that the original normal solution, from which the others are graduated, shall be rigidly exact, otherwise considerable errors will inevitably occur at every step.

Under all circumstances, it is safer to prove the strength of any standard solution by experiment, even though its constituent has been accurately weighed in the dry and pure state.

Further, let us suppose that a solution of caustic soda is to be made by means of lime, as described previously—after pouring off the clear liquid, water is added to the sediment to extract more alkaline solution; by this means we may obtain two solutions, one of which is stronger than necessary, and the other weaker. Instead of mixing them in various proportions and repeatedly trying the strength, we may find, by two experiments and a calculation, the proportions of each necessary to give a normal solution, thus:—

The exact actual strength of each solution is first found by separately running into 10 c.c. of normal acid as much of each alkaline solution as will exactly neutralise it. We have, then, in the case of the stronger solution, a number of c.c. required less than 10. Let us call this number V.

In the weaker solution the number of c.c. is greater than 10, represented by v. A volume of the stronger solution $= x$ will saturate 10 c.c. of normal acid as often as V is contained in x.

A volume of the weaker solution $= y$ will, in like manner, saturate $\frac{10\,y}{v}$ c.c. of normal acid; both together saturate $\frac{10\,x}{V} + \frac{10\,y}{v}$, and the volume of the saturated acid is precisely that of the two liquids, thus—

$$\frac{10x}{V} + \frac{10y}{v} = x + y.$$

Whence

$$10\,vx + 10\,Vy = Vvx + Vvy$$
$$vx\,(10 - V) = Vy\,(v - 10).$$

And lastly,

$$\frac{x}{y} = \frac{V(v - 10)}{v(10 - V)}$$

An example will render this clear. A solution of caustic soda was taken, of which 5·8 c.c. were required to saturate 10 c.c. normal acid; of another solution, 12·7 c.c. were required. The volumes of each necessary to form a normal solution were found as follows:—

$$5{\cdot}8\ (12{\cdot}7 - 10) = 15{\cdot}66$$
$$12{\cdot}7\ (10 \ - 5{\cdot}8) = 53{\cdot}34.$$

Therefore, if the solutions are mixed in the proportion of 15·66 c.c. of the stronger with 53·34 c.c. of the weaker, a correct solution ought to result. This same principle of adjustment is, of course, applicable to standard solutions of every class.

Again, suppose that a standard solution of sulphuric acid has been made approximating as nearly as possible to the normal strength, and its exact value found by precipitation with baric chloride, or a standard hydrochloric acid with argentic nitrate, and such a solution has been calculated to require the coefficient 0·995 to convert it to normal strength,—by the help of this solution, though not strictly normal, we may titrate an approximately normal alkaline solution thus; two trials of the acid and alkaline solutions show that 50 c.c. alkali = 48·5 c.c. acid, having a coefficient of 0·995 = 48·25 c.c. normal; then, according to the equation, x 50 = 48·25 is the required coefficient for the alkali.

$$\frac{48{\cdot}25}{50} = 0{\cdot}965.$$

And here, in the case of the alkaline solution being sodic carbonate, we can bring it to exact normal strength by a calculation based on the equivalent weight of the salt, thus—

$$1 : 0{\cdot}965 :: 53 : 51{\cdot}145.$$

The difference between the two latter numbers is 1·855 gm., and this weight of pure sodic carbonate, added to 1 litre of the solution, will bring it to normal strength.

METHOD OF PROCEDURE IN TITRATING ALKALIES AND ACIDS.

Salts of Soda and Potash.

§ 16. The necessary quantity of substance being weighed or measured, as the case may be, and mixed with distilled water to a proper state of dilution, a sufficient quantity of litmus to produce a distinct blue or red colour is added, and the solution is ready for the burette. Let us suppose that sodic carbonate is to be titrated, the acid from the burette is allowed to flow in until a claret tinge begins to appear. This takes place some time before the complete quantity of acid is added, owing to the liberation of carbonic acid. In order to dissipate the carbonic acid, the liquid must be heated to boiling over a spirit or gas lamp, when the blue colour will again appear. Continue to add the acid a few drops at a time, and repeat the heating until all the carbonic acid is expelled and a distinct pink red colour is produced in the liquid by the final drop of acid. It is always advisable to make a second and conclusive test of the alkali, and, therefore, the first supplies a guide to the quantity of acid required, and allows a more exact method of procedure towards the end of the process.

In the examination of samples of ordinary soda or pearlash, it is advisable to proceed as follows:—

Powder and mix the sample thoroughly, weigh 10 gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture; wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 c.c. with distilled water in a half litre flask, after mixing it thoroughly take out 50 c.c. = 1 gm. of alkali with a pipette, and empty it into a small flask, bring the flask under a burette containing normal acid and graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., allow the acid to flow cautiously as before directed, until the neutral point is reached, the process may then be repeated several times if necessary, in order to be certain of the correctness of the analysis.

As the presence of carbonic acid always tends to confuse the exact end of the process, the difficulty may be overcome by allowing more acid than is needed to flow into the alkali, boiling to expel the carbonic acid, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes to violet blue; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of test acid necessary to saturate the 1 gm. of alkali is ascertained.

This residual or backward method of testing gives a very sharp and sure result, as there is no carbonic acid present to interfere with the colour of the liquid. An example will make the plan clear:—

50 c.c. of the solution of alkali prepared as directed, and which is equal to 1 gm. of the original sample, is put into a flask and exactly 20 c.c. of normal acid allowed to flow into it, it is then boiled and shaken till all carbonic acid is expelled, and normal caustic alkali added backward till the neutral point is reached; the quantity required is 3·4 c.c., which deducted from 20 c.c. of acid, leaves 16·6 c.c. The following calculation, therefore, gives the

percentage of real alkali, supposing it to be soda—31 is the half molecular weight of dry soda, NaO,* and 1 c.c. of the acid is equal to 0·031 gm., therefore, 16·6 c.c. is multiplied by 0·031, which gives 0·5146, and as 1 gm was taken, the decimal point is moved two places to the right, which gives 51·46 per cent. of real alkali; if calculated as carbonate, the 16·6 would be multiplied by 0·053 which gives 0·8798 gm. = 87·98 per cent.

The alkaline salts of commerce, and also alkaline lyes used in soap, paper, starch, and other manufactories, consist generally of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportion in which these mixtures occur, the total alkaline power of a weighed or measured quantity of substance is ascertained by normal acid and noted; a like quantity is then dissolved in about 150 c.c. of water, in a 300 c.c. flask, heated to boiling, and enough solution of baric chloride added to remove all the carbonic acid from the soda or potash; there must be an excess of chloride, but as it does not interfere with the accuracy of the result the exact quantity is of no consequence.

The flask is now filled up to the 300 c.c. mark with distilled water, corked, and put aside to settle. When the supernatant liquid is clear, take out 100 c.c. with a pipette, and titrate with normal nitric acid to the neutral point. The number of c.c. multiplied by 3, will be the quantity of acid required for the caustic alkali in the original weight of substance, because only $\frac{1}{3}$ was taken for analysis.

The precipitated baric carbonate may be thrown upon a filter, washed well with hot water, and titrated with normal nitric acid, as described further on, if the operator chooses, instead of the original analysis for the total alkalinity, or both plans may be adopted as a check upon each other.

The principle of this method is, that when baric chloride is added to a mixture of caustic and carbonated alkali, the carbonic acid of the latter is precipitated as an equivalent of baric carbonate, while the equivalent proportion of caustic alkali remains in solution as baric hydrate. By multiplying the number of c.c. of acid required to saturate this free alkali with the atomic weight of caustic potash or soda, according to the alkali present, the quantity of substance originally present in this state will be ascertained.

As caustic baryta absorbs carbonic acid very readily when exposed to the atmosphere, it is preferable to allow the precipitate of baric carbonate to settle in the flask as here described, rather than to filter the solution as recommended by some operators.

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* The commercial standard often used is 32, (being based on the old erroneous equivalent of Na.)

A slight error, however, always occurs in all such cases in consequence of the precipitate being included in the measured liquid.

AMMONIA.

$NH^3 = 17$.

§ 17. In estimating the strength of solutions of ammonia by the alkalimetric method, it is better to avoid the tedious process of weighing any exact quantity, and to substitute for it the following plan, which is applicable to most liquids for the purpose of ascertaining both their absolute and specific weights.

Let a small and accurately tared flask, beaker, or other convenient vessel be placed upon the balance, and into it 10 c.c. of the ammoniacal solution delivered from a very accurately graduated 10 c.c. pipette. The weight found is, of course, the absolute weight of the liquid in grammes; suppose it to be 9·65 gm., move the decimal point one place to the left, and the specific weight or gravity is at once given (water being 1), which in this case is 0·965.

The 10 c.c., weighing 9·65 gm., is now titrated with normal acid, of which 49 c.c. are required, therefore $49 \times 0{\cdot}017 = 0{\cdot}833$ gm. $NH^3 = 8{\cdot}64$ per cent, of real ammonia; according to Otto's table 9·65 sp. gr., is equal to 8·50 per cent. Ammonic carbonate, and a mixture of the same with bicarbonate, as it most commonly occurs in commerce, may be titrated direct with normal acid for the percentage of real ammonia. The carbonic acid can be determined by precipitating the solution while hot with baric chloride, and when the precipitate is well washed, dissolving it with an excess of normal acid and titrating backward with normal alkali, as described more fully under the head of alkaline earths, the number of c.c. of acid used multiplied by 0·022 (the ½ mol. wt. of CO^2) will give the weight of carbonic acid present in the sample.

It must be borne in mind that this system can only be used properly with tolerably delicate balances and very accurate pipettes. The latter should invariably be tested by taking the sp. gr. of distilled water at 16° C., according to the plan described.

1. Ammonia in combination estimated by displacement with fixed Alkalies.

The apparatus shown in fig. 19 is of great value in determining accurately all the forms of ammonia which can be displaced by soda, potash, or lime, and the gas so evolved collected in a known volume in excess of normal acid, the excess of acid being afterwards found by residual titration with normal alkali.

The little flask, holding about 200 c.c. and placed upon the wire gauze, contains the ammoniacal substance. The tube *d* is filled with strong solution of caustic potash or soda; the large flask holds about a pint, and contains a measured quantity of normal acid, part being contained in the tube *c*, which is filled with broken glass, and through which the normal acid has been poured.

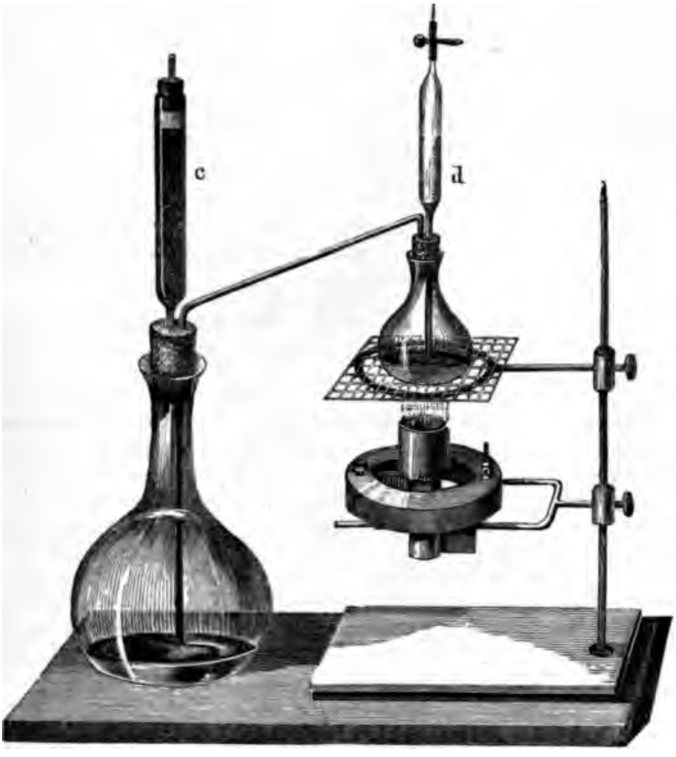

Fig. 19.

The substance to be examined is weighed and put into the distilling flask with a little water, the apparatus then being made tight at every part, some of the caustic alkali is allowed to flow in by opening the clip, and the spirit lamp is lighted under it.

The contents are brought to gentle boiling, taking care that the froth, if any, does not enter the distilling tube. It is well to use a common spirit lamp held under the flask in the hand; in case there is any tendency to boil over, the lamp can be removed immediately and the flask blown upon by the breath, which reduces the pressure in a moment. In examining guano and other substances containing ammoniacal salts and organic matter by this means, the tendency to frothing is considerable, and unless the above precautions are taken, the accuracy of the results will be interfered with.

The distilling tube has both ends cut slantways, and the lower end just reaches to the surface of the acid, to which a little litmus is added. The quantity of acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with normal alkali.

It is advisable to continue the boiling for say ten or fifteen minutes, then wait for the same time to allow all the ammonia to be absorbed. Lastly, boil once or twice for a minute or so, take away the lamp, and allow the apparatus to stand a few minutes to cool; then opening the clip, blow through the pipette so as to force all the remaining gas into the acid vessel. The tube *c* must be washed out into the flask with distilled water, so as to carry down the acid with any combined gas which may have reached it. The titration then proceeds as usual. This process is particularly serviceable for testing commercial ammoniacal salts, gas liquor, &c.; the results are very satisfactory.

Instead of the foregoing direct plan, in the case of tolerably pure neutral ammoniacal salts, a simpler indirect one can be used, which is as follows:—

If the ammoniacal salt be boiled in an open flask with solution of sodic or potassic carbonate, or caustic alkali, the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the strength and quantity of the alkaline solution are known, the excess beyond that, necessary to supplant the ammonia, can be found by the ordinary system of titration. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

Example: 1·5 gm. of purest sublimed ammonic chloride was placed in a flask with 40 c.c. of normal sodic carbonate, and boiled till all ammonia was expelled, then titrated backward with normal sulphuric acid, of which 11·9 c.c. were required; 28·1 c.c. of normal alkali had therefore been neutralized, which multiplied by 0·05346 gave 1·502 gm., instead of 1·5 gm. originally taken.

2. Ammoniacal Gas Liquor.

The value of this substance depends upon the quantity of ammonia contained therein; this constituent mainly exists as carbonate or in a free state, some portion of it, however, generally exists as sulphide and hyposulphite of ammonium. The free and carbonated alkali is best determined by titrating a known volume of the liquor with normal acid and litmus; in consequence of the dark colour and other contaminations of the liquor, it is more secure to ascertain the end of the process by litmus paper—a glass rod or small feather moistened with the mixture may be brought in contact with both red and blue paper, when both remain unaffected the process is finished; each c.c. or dm. of acid is equal to 0·017 gm., or 0·17 grn. of ammonia.

The total quantity of ammonia is ascertained by distilling a portion of the gas liquor in the apparatus, fig. 19. Or an equally exact process, when the liquor contains no other salt than ammonia, consists in saturating a portion of the liquor with pure hydrochloric acid, and evaporating to perfect dryness on the water-bath, then heating the residue to about 120° C. in the sand or air-bath, dissolving in water, filtering and titrating with decinormal silver solution and chromate, as in § 37.

Each c.c. or dm. of $\frac{N}{10}$ silver solution, is equal to 0·0017 gm. or 0·017 grn. of ammonia.

Hydrosulphuric and hyposulphuric acids can be estimated with $\frac{N}{10}$ iodine solution, as in the case of alkali. (§ 38. 1.)

CONVERSION OF NITROGEN IN NITROGENOUS SUBSTANCES INTO AMMONIA, AND ESTIMATION BY PELIGOT'S PROCESS.

§ 18. This process consists in heating a convenient quantity of the dried substance in a combustion tube with soda lime, by which the nitrogen is converted into ammonia, and this latter being led into a measured volume of normal sulphuric, hydrochloric, or nitric acid contained in Will and Varrentrapp's bulb apparatus, combines with its equivalent quantity; the solution is then titrated residually with standard alkali for the excess of acid, and thus the quantity of ammonia found.

As the combustion tube with its arrangements for organic analysis is well known, and described in any of the standard books on general analysis, it is not necessary to give a description here.

Instead of leading the ammonia through normal acid, hydrochloric acid of unknown strength may be used, the liquid brought into the distilling apparatus, and the ammonic chloride estimated by the process described above.

When it is necessary to estimate very minute portions of ammonia, it may be brought into the form of chloride, and estimated by decinormal silver solution, as described, in § 37, or in many cases preferably by **Nessler's** test, described in the section on Water Analysis.

§ 19. TABLE FOR THE SYSTEMATIC ANALYSIS OF ALKALIES, ALKALINE EARTHS AND ACIDS.

Substance.	Formula.	Atomic Weight.	Quantity to be weighed so that 1 c.c. Normal Solution =1 per cent. of substance.	Normal Factor.*
Soda	$Na^{2}O$	62	3·1 gm.	0·031
Sodic Hydrate . .	$NaHO$	40	4·0 gm.	0·040
Sodic Carbonate . .	$Na^{2}CO^{3}$	106	5·3 gm.	0·053
Sodic Bicarbonate .	$NaHCO^{3}$	84	8·4 gm.	0·084
Potash	$K^{2}O$	94	4·7 gm.	0·047
Potassic Hydrate . .	KHO	56	5·6 gm.	0·056
Potassic Carbonate .	$K^{2}CO^{3}$	138	6·9 gm.	0·069
Potassic Bicarbonate	$KHCO^{3}$	100	10·0 gm.	0·100
Ammonia	NH^{3}	17	1·7 gm.	0·017
Ammonic Carbonate	$(NH^{4})^{2}CO^{3}$	96	4·8 gm.	0·048
Lime (Calcic Oxide)	CaO	56	2·8 gm.	0·028
Calcic Hydrate . .	$CaH^{2}O^{2}$	74	3·7 gm.	0·037
Calcic Carbonate . .	$CaCO^{3}$	100	5·0 gm.	0·050
Baric Hydrate . .	$BaH^{2}O^{2}$	171	8·55 gm.	0·0855
Do. (Crystals) .	$BaO^{2}H^{2}(H^{2}O)^{8}$	315	15·75 gm.	0·1575
Baric Carbonate . .	$BaCO^{3}$	197	9·85 gm.	0·0985
Strontia	SrO	103·5	5·175 gm.	0·0575
Strontic Carbonate .	$SrCO^{3}$	147·5	7·375 gm.	0·07375
Magnesia	MgO	40	2·00 gm.	0·022
Magnesic Carbonate	$MgCO^{3}$	84	4·20 gm.	0·042
Nitric Acid . . .	HNO^{3}	63	6·3 gm.	0·063
Hydrochloric Acid .	HCl	36·5	3·65 gm.	0·0365
Sulphuric Acid . .	$H^{2}SO^{4}$	98	4·9 gm.	0·049
Oxalic Acid . . .	$C^{2}O^{4}H^{2}$	126	6·3 gm.	0·063
Acetic Acid . . .	$C^{2}O^{2}H^{4}$	60	6·0 gm.	0·060
Tartaric Acid . . .	$C^{4}O^{6}H^{6}$	150	7·5 gm.	0·075
Citric Acid	$C^{6}O^{7}H^{8}+H^{2}O$	210	7·0 gm.	0·070

* This is the coefficient by which the number of c.c. of normal solution used in any analysis is to be multiplied in order to obtain the amount of pure substance present in the material examined.

If grain weights are used instead of grammes, the decimal point must be moved one place to the right to give the necessary weight for examination; thus sodic carbonate, instead of 5·3 gm., would be 53 grains—the normal factor in this case would also be altered to 0·53.

ALKALINE EARTHS.

§ 20. Normal nitric or hydrochloric acids are the best agents for the titration of the caustic and carbonated alkaline earths, inasmuch as the resulting compounds are all soluble. Nitric acid is preferable on account of its non-volatile character when heated, as all the insoluble forms of these bodies must be estimated by the residual method, that is to say, dissolved first in an excess of normal acid, heated to dispel carbonic acid in the case of carbonates, and the amount of excess found by normal alkali.

The amount of calcic or calcic and magnesic carbonates dissolved in ordinary waters may be very readily, and with tolerable accuracy, found by taking 200 or 300 c.c. of the water, adding about 1 c.c. of cochineal tincture, and titrating cautiously with $\frac{N}{10}$ nitric or sulphuric acid until the original violet colour gives place to yellow red.

A check trial was made by digesting pure calcic carbonate in water charged with carbonic acid gas—by titration 1·05 gm. per litre was found, by evaporation 1·09 gm.; with mixtures of calcic and magnesic carbonates, there will, of course, be no distinction between the two—the whole will be expressed as calcic carbonate, in the same way as by Clark's soap test.

TITRATION OF ACIDS.

§ 21. This operation is simply the reverse of all that has been said of alkalies, and depends upon the same principles as have been explained in alkalimetry.

With free liquid acids such as hydrochloric, sulphuric, or nitric, the strength is generally taken by means of the hydrometer or specific gravity bottle, and the amount of real acid in the sample ascertained by reference to the tables constructed by Otto, Bineau, or Ure. The specific gravity may very easily be taken with the pipette as recommended with ammonia, and of course the real acid may be quickly estimated by normal caustic alkali.

1. Hydrochloric Acid.

HCl.

Example: 5 c.c. of white and tolerably pure hydrochloric acid was put into a small tared bottle, and the weight found to be

5·6 gm.; this divided by 5, gave the sp. gr. as 1·12. It was diluted and titrated with normal alkali, of which 37·1 c.c. were required; this multiplied by 0·0365, gave 1·354 gm. = 24·2%. Ure's table gives 24·46 for the same sp. gr.

In order to ascertain the percentage of hydrochloric acid gas in any sample, it is only necessary to multiply the weight of gas found by normal alkali by 100, and divide by the weight of acid originally taken for analysis; the quotient will be the percentage. Or, simpler than this, if the $\frac{1}{10}$ equivalent in grammes, 3·646 gm., or 1 equivalent in grains, = 36·46 grs., be weighed, the number of c.c. or decems will be the percentage respectively.

2. Nitric Acid.

HNO^3.

Example: 5 c.c. of pure nitric acid weighed 6·075 gm., the sp. gr. was therefore 1·215; the quantity of normal alkali required was 33 c.c., which multiplied by 0·054, gave 1·782 gm. NO^5 = 29·3%. Ure's table gives 29·5% for the same specific gravity.

3. Sulphuric Acid.

H^2SO^4.

Example: 10 c.c. of concentrated white sulphuric acid was weighed, and was found to be 18·25 gm.; sp. gr., therefore, 1·825.

In consequence of the great concentration and high sp. gr. of this acid, it is best to use only 1 or 2 c.c. for analysis; after the specific gravity is taken, 1 c.c. may be titrated, taking care that a very fine and accurate pipette is used for the purpose, or if this is not at hand, it must be weighed direct upon the balance.

2 gm. of the above acid were titrated, and found to require 37 c.c. of normal alkali = 90·65% hydrated acid, which agrees exactly with Bineau's table.

4. Acetic Acid.

$C^2H^4O^2 = 60$.

In consequence of the anomaly existing between the specific gravity of acetic acid and its strength, the hydrometer gives no uniformly reliable indication of the latter, and consequently the volumetric method is peculiarly suitable for ascertaining the value of acetic acid in all its forms. For most technical purposes normal caustic alkali may be used as the saturating agent; but a slight error occurs in this method, from the fact that neutral acetates have an alkaline reaction on litmus; the error, however, is very small, if care be taken to add the alkali till a distinct blue colour is reached. As acetic acid is volatile at high temperatures, normal carbonate of soda must not be used for titrating it, as it would necessitate heat to expel the carbonic acid.

Example: 5 c.c. of Beaufoy's acetic acid weighed 5·206 gm. = 1·041 sp. gr. The quantity of normal alkali required to saturate it was 27·1 c.c., which multiplied by 0.06 = 1·626 gm. acetic acid, or 32·5%. For the ordinary vinegars there is no necessity to take the specific gravity into the question; 5 or 10 c.c. may be taken as 5 or 10 gm. Malt or coloured vinegar must be copiously diluted, in order that the change in the colour of the litmus may be distinguished; where the colour is such as to make the end of the process doubtful, recourse must be had to litmus paper, upon which little streaks should be made from time to time with a fine glass rod or a small feather.

Several processes have at various times been suggested for the accurate and ready estimation of acetic acid, among which I may mention that of C. Greville Williams, by means of a standard solution of lime syrup; the results he obtained seemed very satisfactory; but where absolute accuracy is required in every possible form and colour of acetic acid, C. Mohr's process is undoubtedly the most reliable.

It consists in adding to a known quantity of the acid a known excessive quantity of baric or calcic carbonate in fine powder; the pure calcic carbonate described in the chapter on alkaline earths is preferable, as it dissolves more readily than the baryta. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the carbonic acid, and to complete the saturation; the residual carbonate is then brought upon a filter, washed with boiling water, and titrated with normal acid and alkali.

This process is applicable in all cases, and however dark the colour may be; in testing the impure brown pyroligneous acid it is especially serviceable. Pettenkofer titrates acetic acid or vinegar with a known excess of baryta water, and estimates the excess of the latter with $\frac{N}{10}$ nitric or oxalic acid by the help of turmeric paper.

The titration of acetic acid or vinegar may also be performed by Kieffer's ammonio-cupric solution described further on.

PETTENKOFER'S METHOD OF ACIDIMETRY,

Especially serviceable for free carbonic acid and coloured acid liquids, such as commercial vinegars, &c.

§ 22. The special feature of this process is the use of baryta water as the saturating alkali, turmeric paper being used as the indicator. If this paper be made and preserved with care, it admits of very sharp and decisive results as to the point of neutrality in acidimetric testing.

The solution of caustic baryta is best made from the crystallized hydrate, it is not advisable to have the solution too concentrated, since when it is near complete saturation it is apt to deposit the hydrate at low temperatures. The corresponding acid may be either $\frac{N}{10}$ oxalic, nitric, or hydrochloric; oxalic acid is recommended by Pettenkofer for carbonic acid estimation, because it has no effect upon the baric carbonate suspended in weak solutions; but there is the serious drawback in oxalic acid that in dilute solution it is liable to decomposition, and as in my experience $\frac{N}{10}$ hydrochloric acid in dilute mixtures has no effect upon the suspended baric carbonate, it is preferable to use this acid.

The baryta solution is liable to constant change by absorption of carbonic acid, but this may be prevented to a great extent by preserving it in the bottle shown in fig. 17. A thin layer of petroleum oil on the surface of the liquid preserves the baryta at one strength for a long period.

The use of turmeric paper with baryta gives, in my opinion, by far the most delicate reaction of all the indicators used in testing acids or alkalies.

The merest trace of baryta in excess gives a decided brown tinge to the edge of the spot made by a glass rod on the turmeric paper. If the substance to be tested is not too highly coloured, litmus may be used as an approximate indicator in the mixture, this enables the operator to find the exact point of saturation more conveniently.

KIEFFER'S NORMAL AMMONIO-CUPRIC SOLUTION FOR ACIDIMETRY.

§ 23. This acidimetric solution is prepared by dissolving pure cupric sulphate in warm water, and adding to the clear solution liquid ammonia, until the bluish green precipitate which first appears is nearly dissolved; the solution is then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c. into 10 or 20 c.c. of normal sulphuric or nitric acid (not oxalic); while the acid remains in excess, the bluish green precipitate which occurs as the drop falls into the acid rapidly disappears; but so soon as the exact point of saturation occurs, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid.

The process is especially serviceable for the estimation of the free acid existing in certain metallic solutions, *i.e.*, mother liquors, &c., where the neutral compounds of such metals have an acid reaction on litmus—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel; it is also applicable to acetic and the mineral acids.

The value of the process in any given case depends upon the insolubility of the cupric oxide in the neutral solution which results from the combination of the ammonia and acid. **Carey Lea** (*vide* "Chemical News," Oct. 12th, 1861, p. 196) has objected to this process on the ground that the precipitate (which he supposes to be a basic sulphate of copper) is not totally insoluble in certain neutral solutions when concentrated, such as ammonic sulphate, nitrate, or chloride, and he thinks it strange that so experienced a chemist as **Mohr** should be led into the error of highly recommending such an acidimetrical process, alleging that a different result would be obtained between testing a solution containing 5 gm. of sulphuric acid with 5 gm. of ammonic sulphate, and the same quantity of acid with 20 or 50 gm. of ammonic sulphate. On this ground the objection is true, owing to the soluble effect exerted by large excesses of ammoniacal salts; but, on the other hand, such excesses are not likely to occur, or must be avoided. **Fresenius** and **Mohr** both recommend the process for technical purposes.

If cupric nitrate be used for preparing the solution instead of sulphate, the presence of barium, or strontium, or metals precipitable by sulphuric acid, is of no consequence. The solution is standardised by normal nitric or sulphuric acid, and as it slightly alters by keeping, a coefficient must be found from time to time by titrating with normal acid, by which to calculate the results systematically; oxides or carbonates of magnesia, zinc, or other admissible metals, are dissolved in excess of normal nitric acid, and titrated residually with the copper solution.

Example: 1 gm. pure oxide of zinc was dissolved in 27 c.c. normal acid, and 2·3 c.c. normal copper solution required to produce the precipitate = 24·7 c.c. acid; this multiplied by 0·0405, the coefficient for monobasic zinc gave 1·001 gm.

3·9 gm. Howard's calcined magnesia were dissolved in 220 c.c. normal sulphuric acid and 30 c.c. copper solution were required, whose factor for normal strength was 0·909 = 27·27 c.c. normal; this deducted from 220 c.c. leaves 192·73 c.c. = 3·86 gm. pure magnesia, or 99%. Mother liquors, mixed acids of the galvanic battery containing metals, &c., can be examined for the amount of free acid by this means; so also may acetic acid or vinegar, the only necessary condition being that the acid shall be very dilute, as the copper precipitate is soluble in concentrated cupric acetate; if the first drop of copper solution produces a turbidity which disappears only on shaking or stirring the liquid, the dilution is sufficient. In order that the first traces of a permanent precipitate may be recognised, it is well to place a piece of dark coloured paper under the beaker. The results are very uniform and reliable.

For the vinegars of commerce this process seems peculiarly applicable, as a large amount of dilution is of no consequence.

CARBONIC ACID AND CARBONATES.

§ 24. All carbonates are decomposed by strong acids; the carbonic acid which is liberated splits up into water and carbonic anhydride (CO^2), which latter escapes in the gaseous form.

It will be readily seen from what has been said previously as to the estimation of the alkaline earths, that carbonic acid in combination with a great variety of cases can be estimated volumetrically with a very high degree of accuracy.

The carbonic acid to be estimated may be brought into combination with either calcium or barium, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exists in a soluble form as an alkaline monocarbonate, the decomposition is effected by the addition of baric or calcic chloride as before directed; if as bicarbonate, or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia most frequently contains carbonic acid, it must be removed by the aid of baric or calcic chloride previous to use, should there be any present. It may be kept from absorbing carbonic acid by means of the tube described for normal alkali.

Example: 1 gm. of pure anhydrous sodic carbonate was dissolved in water, precipitated while hot with baric chloride, the precipitate filtered off and washed thoroughly with boiling water, the filter and precipitate were then placed in a flask, and 26 c.c. of normal nitric acid added, then titrated with normal alkali, of which 7·2 c.c. were required = 18·8 c.c. of acid; this multiplied by 0·022, the coefficient for monobasic carbonic acid, gave 0·4136 gm. CO^2 = 41·36 per cent. or multiplied by 0·053, the coefficient for monobasic sodic carbonate gave 0·9964 gm. instead of 1 gm.

1 gm. of pure and dry sodic bicarbonate in powder was dissolved and precipitated with ammonia and calcic chloride, the precipitate washed with boiling water till all ammonia was removed, the precipitate and filter then titrated with normal acid and alkali; the quantity of acid used was 23·5 c.c. = 51·7 per cent. of CO^2; the percentage, supposing the salt to be absolutely pure, would be 52·3.

There seems to be no difference, with respect to accuracy, between calcic or baric chloride as the precipitant; but as the calcic carbonate can be more readily washed without clogging the filter, it is preferable to use that substance.

It sometimes occurs that substances have to be examined for carbonic acid, which do not admit of being treated as above described; such, for instance, as the carbonates of the metallic oxides, (white lead, calamine, &c.), carbonates of magnesia, iron, and copper, the estimation of carbonic acid in cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with calcic chloride, and titrated as before described.

The following form of apparatus (fig. 20) affords satisfactory results.

It is the same arrangement in principle as shown in fig. 19 for the distillation of ammonia, with the exception that the flask *b* and tube *d* are somewhat larger, and are placed on a level with the larger flask.

The weighed substance from which the carbonic acid is to be evolved is placed in *b* with a little water and litmus; the tube *d* contains strong hydrochloric acid, and *c*, broken glass wetted with ammonia free from carbonic acid. (This should be heated with a little calcic chloride in a test tube; if pure, it will remain clear.) The flask *a* is about one-eighth filled with the same ammonia, the bent tube must not enter the liquid. When all is ready and the corks tight (best secured by wetting them,) warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow circumspectly upon the material, which may be heated until all carbonic acid is apparently driven off, then by boiling and shaking the last traces can be evolved and the operation ended. When cool, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c* so as to carry down any ammonic carbonate that may have formed. Then add solution of calcic chloride, boil, filter, and titrate the precipitate, as before described.

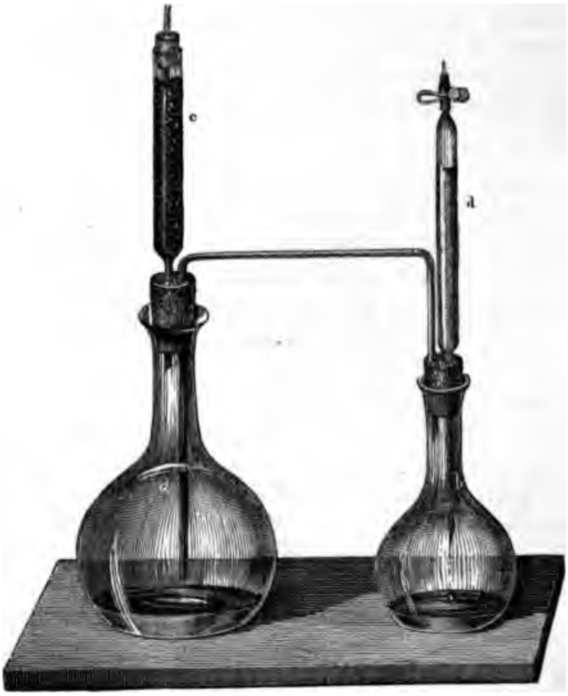

Fig. 20.

During the filtration, and while ammonia is present, there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

In many instances CO^2 may be estimated by its equivalent in chlorine with $\frac{N}{10}$ silver and potassic chromate as shown in § 37. It may also be collected in the gaseous form and measured as described in Part VII.

1. Carbonic Acid Gas in Waters, &c.

Well or spring water, and also mineral waters containing free carbonic acid gas, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of calcic and ammonic chloride, afterwards boiling the mixture and titrating the precipitate as usual.

Pettenkofer's method with caustic baryta or lime as previously described is decidedly preferable to any other. The baryta solution should be preserved in the bottle shown in fig. 17. Lime water may be used instead of baryta with equally good results for very small quantities of carbonic acid.

The principle of the method is that of removing all the carbonic acid from a solution or from a water, by excess of baryta or lime water of a known strength, and after absorption finding the excess of baryta or lime by titration with weak standard acid.

The following is the best method to be pursued for ordinary drinking waters not containing large quantities of carbonic acid:—

500 c.c. of the water are put into a flask with a measured quantity of weak baryta or lime water, the strength of which is previously ascertained by means of decinormal acid, then boiled, well corked, and put aside to cool and settle; when cold and the precipitate subsided, take out 300 c.c. of the clear liquid with a pipette, or pour it off without disturbing the sediment. Let this be titrated with decinormal acid; the quantity required must be calculated for the total water and baryta or lime solution, there being 300 c.c. only taken; the number of c.c. so found must be deducted from the original quantity required for the baryta solution added; the remainder multiplied by 0·0022 (the acid being decinormal,) will give the weight of carbonic acid in the 500 c.c. free and as bicarbonate.

By collecting the precipitate, and titrating it as previously described, the total carbonic acid may be found.

Example: 500 c.c. spring water were mixed with 30 c.c. baryta water = 34·5 c.c. $\frac{N}{10}$ hydrochloric acid, boiled, corked, and set aside to cool; 300 c.c. of the clear liquid titrated with $\frac{N}{10}$ acid, of which 6·5 c.c. were required, consequently the 530 c.c. required 11·5 c.c.; this deducted from 54·5 c.c., the quantity required for the 30 c.c. baryta solution, leaves 43 c.c. $\frac{N}{10}$ acid, which multiplied by 0·0022, gives 0·0946 gm. CO^2, in the 500 c.c. of water, free and as bicarbonate.

The precipitate required 8·4 c.c. normal nitric acid = 0·1848 gm. CO^2, which is the total weight combined and free; consequently the following calculation will give the results in detail.

Total CO^2	0·1848 gm.
Deduct free and as bicarbonate	0·0946 ,,
Leaving combined ...	0·0902 ,,

The weight of CO^2, as bicarbonate, will, of course be equal to this, and the two = 0·1804 gm., which deducted from 0·1848 gm. gives free CO^2 = 0·0044 gm. Thus

Free CO^2	0·0044 gm.
Do. as bicarbonate	0·0902 ,,
Do. as neutral carbonate	0·0902 ,,
Total	0·1848 ,, CO^2

If the water contains magnesia, some solution of ammonic chloride must be added to prevent its precipitation by the baryta; and instead of boiling, which would decompose and dissipate the ammonia, the flask should be closely stoppered and digested in hot water; when perfectly cold and clear the examination may be completed as above. If it be desirable to ascertain the volume of carbonic acid from the weight, 1000 c.c. of gas, at 0° and 0·76 mm., weigh 1·96663 gm. 100 cubic inches weigh 47·26 grains.

For ascertaining the quantity of carbonic acid in bottled aërated waters, such as soda, seltzer, potass, and others, the following apparatus is useful. Fig. 21 is a brass tube made like a corkborer about five inches long, having four small holes, two on each side, at about two inches from its cutting end; the

Fig. 21.

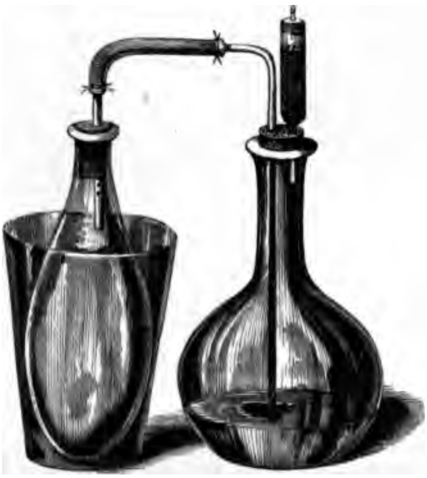

Fig. 22.

upper end is securely connected with the bent tube from the absorption flask (fig. 22,) by means of a vulcanised tube; the flask contains a tolerable quantity of pure ammonia into which the delivery tube dips; the tube *a* contains broken glass moistened with ammonia.

Everything being ready the brass tube is greased with tallow or paraffin, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork by turning the bottle round, until the holes appear below the cork and the gas escapes into the flask. When all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can be possibly eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also; the whole is then precipitated with calcic chloride and boiled, and the precipitate titrated as usual. This gives the total carbonic acid free and combined.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of carbonic acid in the monocarbonate deducted from the total will give the weight of gas originally present.

The volume may be found as follows:—1000 c.c. of carbonic acid at 0°, and 76 mm., weigh 1·96663 gm. Suppose, therefore, that the total weight of carbonic acid found in a bottle of ordinary soda water was 2·8 gm., and the weight combined with alkali 0·42 gm., this leaves 2·38 gm. CO^2 in a free state—

$$1·96663 : 2·38 :: 1000 : x = 1210 \text{ c.c.}$$

If the number of c.c. of carbonic acid found is divided by the number of c.c. of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. In this case the volume of the contents of the bottle was ascertained by marking the height of the fluid previous to making the experiment; the bottle was afterwards filled to the same mark with water, which was emptied into a graduated cylinder, and found to measure 292 c.c., therefore

$$\frac{1210}{292} = 4·14 \text{ vols. } CO^2.$$

2. Carbonic Acid in Air.

A glass globe or bottle capable of being securely closed by a stopper or otherwise, and holding 4 to 6 litres, is filled with the air to be tested by means of a bellows aspirator—baryta water is then introduced in convenient quantity and of known strength as compared with $\frac{N}{10}$ acid. The vessel is securely closed and the liquid allowed to flow round the sides at intervals during half-an-hour; if at the end of that time no great amount of cloudiness in the baryta has occurred, it may be advisable to refill the bottle with air one or more times, this can of course be done with the aspirator as at first, taking care on each occasion to agitate the vessel so as to bring the baryta in contact with all parts of its surface during the space of half-an-hour. When sufficient air has thus been treated, the baryta is emptied out quickly into a beaker, the bottle rinsed out with distilled water free from CO^2, the rinsings added to the baryta and the excess of the latter at once ascertained by $\frac{N}{10}$ hydrochloric acid and turmeric paper as described in § 22; or instead of taking the whole of the bartya, that and the rinsings may be emptied into a stoppered cylinder, made up to a definite measure and half or one third taken for titration—the final calculation is of course made on the total baryta originally used and upon the exact measurement of the air-collecting vessel.

A convenient method of calculation is to convert the volume of baryta solution decomposed, into its equivalent volume in $\frac{N}{10}$ acid, 1 c.c. of which = 0·0022 gm. CO^2, or by measurement at 0°C and 760 m.m. pressure represents 1·119 c.c.

ESTIMATION OF COMBINED ACIDS IN NEUTRAL SALTS.

§ 25. This comprehensive method of determining the quantity of acid in neutral compounds (but not the nature of the acid), is applicable only in those cases where the base is perfectly precipitated by an excess of caustic alkali or its carbonate. The number of bodies capable of being so precipitated is very large, as has been proved by the researches of MM. Langer and Wawnikiewicz, (Ann. der Chemie und Pharm., p. 239, Feb. 1861), who seem to have worked out the method very carefully. These gentlemen attribute its origin to Bunsen; but it does not seem certain who devised it. The best method of procedure is as follows :—

The substance is weighed, dissolved in water in a 300 c.c. flask, heated to boiling or not, as may be desirable, normal alkali or its carbonate, according to the nature of the base, is then added, from a burette, until the whole is decidedly alkaline. It is then diluted to 300 c.c. and put aside to settle, and 100 c.c. are taken out and titrated for the excess of alkali; the remainder multiplied by 3, gives the measure of the acid combined with the original salt, *i.e.*, supposing the precipitation is complete.

Example: 2 gm. crystals of baric chloride were dissolved in water, heated to boiling, and 20 c.c. normal sodic carbonate added, diluted to 300 c.c., and 100 c.c. of the clear liquid titrated with normal nitric acid, of which 1·2 c.c. were required—altogether, therefore, the 2 gm. required 16·4 c.c. normal alkali; this multiplied by 0·122, gave 2·0008 gm. Ba Cl^2, instead of 2 gm.; multiplied by the factor for chlorine 0·03546, it yielded 0·58154 gm., theory requires 0·5813 gm. chlorine.

The following substances have been submitted to this mode of examination with satisfactory results:—

Salts of the alkaline earths precipitated with an alkaline carbonate while boiling hot.

Salts of magnesia, with pure or carbonated alkali.

Alum, with carbonate of alkali.

Zinc salts, boiling hot, with the same.

Copper salts, boiling hot, with pure potash.

Silver salts, with same.

Bismuth salts, half-an-hour's boiling, with sodic carbonate.

Nickel and Cobalt salts, with the same.

Lead salts, with the same.

Iron salts, boiling hot, with pure or carbonated alkali.

Mercury salts, with pure alkali.

Protosalts of manganese, boiling hot, with sodic carbonate.

Chromium persalts, boiling hot, with pure potash.

Where the compound under examination contains but one base precipitable by alkali, the determination of the acid gives, of course, the quantity of base also.

Wolcott Gibbs (Chem. News, vol. i., 1868, p. 151) has enunciated a new acidimetric principle applicable in cases where a base is precipitable at a boiling temperature by hydric sulphide, and the acid set free so as to be estimated with standard alkali. Of course the method can only be used where complete separation can be obtained, and where the salt to be analysed contains a fixed acid which has no effect upon hydric sulphide. A weighed portion is dissolved in water, brought to boiling, and the gas passed in until the metal is completely precipitated, which is known by testing a drop of the clear liquid upon a porcelain tile with sulphuretted hydrogen water, or any other appropriate agent adapted to the metallic salt under examination.

The liquid is filtered from the precipitate, and the latter well washed, and the solution made up to a definite measure. An aliquot portion is then titrated with normal alkali and litmus as usual.

In the case of nitrates or chlorides, where nitric or hydrochloric acid would interfere with the hydric sulphide, it was found that the addition in tolerable quantity of a neutral salt containing an organic acid (*e.g.*, sodic or potassic tartrate, or the double salt) obviated all difficulty.

The results obtained by Gibbs in the case of copper, lead, bismuth, and mercury, as sulphate, nitrate, and chloride, agreed very closely with theory; but the process would be very objectionable to many on account of the offensive and poisonous character of the gas necessarily employed in the precipitation.

ESTIMATION OF SULPHURIC ACID, BARYTA, CHLORINE, IODINE, AND BROMINE INDIRECTLY.

§ 26. Bohlig (Fresenius' Zeitschrift, 1870, p. 310) has described a method for estimating these bodies, which appears worthy of some consideration, since the only standard solutions required are an acid and an alkali.

The following summary of the process is from the Chemical Society's Quarterly Journal, 1871, page 436:—

Alkaline sulphates are known to be partially decomposed, in contact with baric carbonate, into alkaline carbonates and baric sulphate. The decomposition is complete in the presence of free carbonic anhydride; acid carbonates of the alkali-metals are left in solution, together with some acid baric carbonate, which can be removed by boiling. The solution is filtered, and the alkaline carbonate determined by means of a standard acid solution, and the amount of sulphuric acid or alkaline sulphate calculated from the amount of normal acid required.

Neutral chlorides, bromides, and iodides, more especially of the alkali-metals, are most readily decomposed by pure silver oxide into insoluble silver salts, leaving the alkali-metal in solution as hydrate (ammonia salts always excepted) which can then be determined as usual by standard acid.

The author treats solutions containing sulphates of the heavy metals, of the earths or alkaline earths (lime), and free from acids whose presence would influence the method, viz., phosphoric, arsenic, oxalic, &c., with a solution of potassic carbonate so as to precipitate the bases and leave about double or treble the amount of alkaline carbonate in solution. From 1 to 1½ grm. of substance is operated upon in a flask. The solution is made up to 500 c.c.

well shaken, and the precipitate allowed to subside. 50 c.c. are then filtered into a porcelain dish and heated to boiling, and standard acid (HCl) added to neutralisation. Another 100 c.c. are filtered in like manner, into a strong quarter-litre flask, and diluted with about 100 c.c. of hot water; the requisite quantity of normal acid is then run in at once from a burette; the solution diluted to 250 c.c.; and about a gramme of dry barium carbonate (free from alkali) added. The flask is next closed and the liquid well agitated. The decomposition of the alkaline sulphate is complete in a few minutes. The flask should be opened now and then to allow the carbonic anhydride to escape. Finally, about ½ grm. of pulverised barium hydrate is added, the whole well shaken, and a portion of the rapidly clearing liquid tested qualitatively for barium and sulphuric acid. The result should be a negative one. 50 c.c. corresponding to 20 c.c. of the original solution are then filtered into a porcelain dish and standardized with normal acid (hydrochloric or sulphuric), and the quantity of sulphuric acid (sulphate) calculated as usual.

The source of carbonic anhydride is thus placed in the liquid itself, provided the quantity of potassic carbonate be not too small.

Equivalent quantities of $K^2SO^4 + 2K^2CO^3 + 2HCl + BaCO^3$ when mixed with sufficient water, change into $BaSO^4 + 2KHCO^3 + 2KCl$, and it is therefore more than sufficient to add twice the quantity of potassic carbonate compared with the alkaline sulphate operated upon.

Barium hydrate is added with a view of removing any carbonic anhydride left in the liquid after boiling, which would otherwise dissolve some of the excess of baric carbonate contained in the precipitate.

Any baric hydrate not required to remove CO^2 is acted upon by the acid potassic carbonate, but does not influence the final result.

Phosphoric and oxalic acids the author proposes to remove by means of calcium chloride, chromic acid by deoxidising agents, such as alcohol and hydrochloric acid. Bohlig recommends this method for estimating sulphuric acid volumetrically in ashes, crude soda, Stassfurth salts, &c.

Solutions containing baryta are estimated in like manner by precipitation as carbonate, and decomposition with potassium sulphate in a solution containing free carbonic acid. Chlorine is determined volumetrically in solutions by first precipitating any metallic chloride with potassic carbonate added in moderate excess.

The filtrate is made up to 250 c.c. and the excess of potassic carbonate determined in 50 c.c. by means of a normal solution of HCl. 125 c.c. of the solution are next treated with excess of silver oxide and made up to 250 c.c., well shaken (out of contact with the light) and filtered. 100 c.c. of the filtrate are standardized with normal hydrochloric acid. The difference between the quantity of acid required in the last and that of the first experiment, multiplied by 5, gives the amount of chlorine contained in the original solution. A portion of the filtrate should be tested for chlorine by means of mercurous nitrate.

The filtrate is obtained perfectly clear only in the presence of some potassic or sodic carbonate, and by employing argentic oxide free from argentous oxide. A few drops of pure potassium permanganate added to the argentic oxide preserved in water prevent formation of the latter. The oxide to be employed for each experiment is filtered when required, and thoroughly washed.

Bromine and iodine are determined in like manner. The author has not been able, however, to estimate the mixtures of the halogen salts ; but he has made the interesting observation that potassium iodide, when boiled with potassium permanganate is completely oxidised into iodate. This facilitates the detection of small quantities of chlorine and bromine, in the presence of much iodide. The greater part of iodate may be separated also by precipitation with baric nitrate before determining chlorine. The standard acid solutions which Bohlig employed contained not more than one-third of the equivalent of HCl or SO^3 per litre.

For further particulars the reader is referred to the original paper (Arch. Pharm. 3, cxlv, 113).

PART III.

ANALYSIS BY OXIDATION OR REDUCTION.

INTRODUCTION.

§ 27. THE series of analyses which occur under this system are very extensive in number, and not a few of them possess extreme accuracy, such in fact, as is not possible in any analysis by weight, The completion of the various processes is generally shown by a distinct change of colour—such, for instance, as the occurrence of the beautiful rose red permanganate, or the blue iodide of starch; and as the smallest quantity of these substances will colour distinctly large masses of liquid, the slightest excess of the oxidising agent is sufficient to produce a distinct effect.

The principle involved in the process is extremely simple. Substances which will take up oxygen are brought into solution, and titrated with a substance of known oxidising power—as, for instance, in the determination of ferrous salts by permanganic acid. The iron is ready and willing to receive the oxygen, the permanganate is equally willing to part with it; while the iron is absorbing the oxygen, the permanganate loses its colour almost as soon as it is added, and the whole mixture is colourless, but immediately the iron is satisfied, the rose colour no longer disappears, there being no more oxidisable iron present. In the case of potassic permanganate the reaction is; $10\ FeO + 2\ MnKO^4 = 5\ Fe^2O^3 + 2\ MnO + K^2O$. Oxalic acid occupies the same position as the ferrous salts, its composition is $C^2O^4H^2 + 2H^2O = 126$; if permanganate is added to it in acid solution, the oxalic acid is oxidised to carbonic acid, and the manganic reduced to manganous oxide, thus $Mn^2O^7 + 5C^2O^4H^2 + 2H^2SO^4 = 10CO^2 + 2MnSO^4 + 7H^2O$; when the oxalic acid is all decomposed the colour of the permanganate no longer disappears. On the other hand, substances which will give up oxygen are deoxidised by a known excessive quantity of reducing agent, the amount of which excess is afterwards ascertained by residual titration with a standard oxidising solution; the strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The oxidising agents best available are—potassic permanganate, iodine, potassic bichromate, and red potassic prussiate.

The reducing agents are—sulphurous acid, sodic hyposulphite, oxalic acid, ferrous oxide, arsenious anhydride, stannous chloride, yellow potassic prussiate and zinc.

With this variety of materials a great many combinations may be arranged so as to make this system of analysis very comprehensive, but the following are given as sufficient for almost all purposes, and as being susceptible of the greatest amount of purity and stability of material, with exceedingly accurate results :—

1. Permanganate and ferrous salts (with the rose colour as indicator); permanganate and oxalic acid (with the rose colour as indicator).
2. Potassic bichromate and ferrous salts (with cessation of blue colour when brought in contact with red potassic prussiate, as indicator).
3. Iodine and sodic hyposulphite (with starch as indicator); iodine and sodic arsenite (with starch as indicator).

PREPARATION OF STANDARD SOLUTIONS.

PERMANGANIC ACID AND FERROUS OXIDE.

1. Potassic Permanganate.

$MnKO^4 = 158$. Decinormal Solution = 3·16 gm. per litre.

§ 28. The solution of this salt is best prepared for analysis by dissolving the pure crystals in distilled water of such a strength that 17·85 c.c. will peroxidise 1 decigramme of iron. The solution is then decinormal. If well kept, it will retain its strength for several months.

If the salt can be had perfectly pure and dry, 3·16 gm. dissolved in a litre of water at 16° C. will give an exactly decinormal solution; but, nevertheless, it is always well to titrate it upon a definite quantity of iron or oxalic acid.

A very useful form of bottle for preserving it is that shown in fig. 17. Burettes can then be filled with the solution without frothing. The cork in the tubulure must, however, be well soaked in melted paraffine.

The solution may also be kept in any good stoppered bottle, and while it is quite free from sediment, it may be taken for granted that its strength is unaltered.

2. Titration of Permanganate with Ammonio-ferrous Sulphate.

In order to ascertain the strength of the permanganate it must be titrated with either a weighed quantity of metallic iron, oxalic acid, or the double sulphate of iron and ammonia.

This latter salt is a most convenient substance for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and being perfectly stable when pure, it can be depended on without risk. To prepare it, 139 parts of the purest crystals of ferrous sulphate, and 66 parts of pure crystallised ammonic sulphate are separately dissolved in the least possible quantity of distilled water of about 40° C., if the solutions are not perfectly clear they must be filtered; mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold, during the stirring the double salt will fall in a finely granulated form, set aside for a few hours, then pour off the supernatant liquor, and empty the salt into a clean funnel with a little cotton wool stuffed into the neck, so that the mother liquor may drain away; the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper, or still better, as Mohr recommends, dried in a centrifugal machine. As very few persons are possessed of this latter, albeit a most useful article, the salt may be spread out on a tray made of filtering paper, and the superfluous moisture driven off by a fan or pair of bellows; lastly, place it in a current of air to dry thoroughly so that the small grains adhere no longer to each other or to the paper in which they are contained, then preserve in a stoppered bottle for use. It is constantly being stated in books that this salt does not keep of uniform constitution—if so it simply arises from imperfect preparation. If thoroughly dried in air at ordinary temperatures so that the grains do not adhere to each other when placed in a bottle or on paper it remains the same for years.

The formula of the salt is—$Fe(NH^4)^2 (SO^4)^2, 6H^2O = 392$.

Consequently it contains exactly one-seventh of its weight of iron, therefore, 0·7 gm. represent 0·1 gm. of iron, and this is a convenient quantity to weigh for the purpose of titrating the permanganate, or an exact decinormal solution may be made by dissolving 39·2 gm. in a litre of water with the addition of 10 c.c. pure sulphuric acid, and preserving in the bottle (fig. 17).

0·7 gm. being brought into dilute solution in a flask or beaker, and 5 or 6 c.c. of dilute sulphuric acid (1 to 5) added, (the titration of permanganate, or any other substance, by it should always take place in the presence of free acid and preferably sulphuric), the permanganate is delivered from a Gay Lussac's burette or the burette with glass tap divided in $\frac{1}{5}$ or $\frac{1}{10}$ c.c., until a point occurs, when the rose colour no longer disappears on shaking; a few drops of the permanganate in excess are sufficient to produce this effect, but the actual quantity required to colour the same quantity of water should be found, and deducted from the total used in the analysis. The titration is now ended, and should the quantity not be strictly correct, the number of c.c. used may be marked upon the bottle as the quantity for 0·1 gm. Fe, or the factor found, which is necessary to reduce it to decinormal strength, or if too strong, it may be diluted to that strength at once.

3. Titration with Metallic Iron.

The purest iron to be obtained is thin annealed binding-wire free from rust.

About 0·1 gm. of this is to be dissolved in dilute sulphuric acid by the aid of heat, in a small flask closed with a cork, through which a fine glass tube is passed, so that the hydrogen which is evolved escapes under pressure, thus preventing the access of air; or better then this, the plan suggested by Mohr may be used, which consists in passing the upper end of the fine tube through a cork, and laying over the end of the glass tube, which is level with the cork, a small piece of sheet india rubber or oiled silk pinned down to the cork with a pin on each side of the hole. This contrivance acts as a valve by which the hydrogen escapes from the flask under pressure, but so soon as the flask cools, and the pressure of gas ceases, the valve closes by atmospheric pressure and thus prevents the entrance of air; by this means there is no difficulty in obtaining the whole of the iron in solution as protoxide. When the iron is all dissolved the flask may be two-thirds filled with cold distilled water, and the titration with permanganate commenced and concluded as in the case of the double sulphate.

The decomposition which ensues from titrating ferrous oxide by permanganic acid may be represented as follows:—

$$10FeO \text{ and } Mn^2O^7 = 2MnO \text{ and } 5Fe^2O^3,$$

4. Titration with Oxalic Acid.

0·63 gm. of the pure acid is to be weighed, or 10 c.c. of normal solution measured with a pipette, brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 58° C., and the permanganate added from the burette. The colour disappears slowly at first but afterwards more rapidly, becoming first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid, nevertheless, it is as reliable with care and attention.

5. Precautions.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting manganous oxide in solution. Sulphuric acid, in a dilute form, has no prejudicial effect on the pure permanganate, even at a high temperature ; not so, however, nitric or hydrochloric acids, the former, though very dilute, if it contain the lower oxides of nitrogen, immediately decomposes the solution, consequently the last traces of these must be removed by boiling previous to its addition. With hydrochloric acid the solution to be titrated must be very dilute and of low temperature, otherwise chlorine will be liberated and the analysis spoiled; this acid acts as a reducing agent on permanganate in concentrated solution, thus

$$Mn^2O^7 + 14HCl = 7H^2O + 10Cl + 2MnCl^2.$$

Under any circumstances, with this acid the analysis must be subjected to correction, as will be shown further on.

Organic matter of any kind decomposes the permanganate, and the solution, therefore, cannot be filtered through paper, nor can it be used in Mohr's burette, because it is decomposed by the india rubber tube. It may, however, be filtered through gun cotton.

The determination of iron by permanganate, under many circumstances hitherto recommended, is subject to great error, so great, in fact, that the determination may be totally worthless unless subjected to correction.

In Fresenius' "Zeitschrift für Analytische Chemie," (part 3, Oct. 1862.) Löwenthal and Lenssen have contributed a valuable paper on the subject, a short summary of which is as follows. A complete series of determinations of iron was made with different quantities of free hydrochloric and sulphuric acids, with variable quantities of water, free from air and containing air and at various temperatures, correction being in all cases made for the quantity of solution of permanganate necessary to colour the various bulks of liquid.

The results proved conclusively that the process was exact only when the iron existed as sulphate, when a moderate quantity of free sulphuric acid was present, and when deduction was made for the colouration of the liquid. Fresenius has also most carefully checked the statements made by Löwenthal and Lenssen, obtaining results which point to the same conclusion. It is not necessary to give the experiments of Fresenius in detail. The permanganate solution was prepared with the pure crystals and of such strength that 100 c.c.=0·4 gm. iron. The iron solution was prepared from pure sulphate. The hydrochloric and sulphuric acids used were absolutely pure, the first of 1·12 spec. grav., the last of 1·23; fresh distilled water was used for the dilution, and in order to remove any traces of reducing agents it was acidified with sulphuric acid, and sufficient permanganate added to give a permanent pinkish colour. The correction, therefore, for coloration of the liquid was unnecessary.

The variation in quantity of permanganate required for 10 c.c. of iron solution was from 12·6 to 14·3 c.c., the difference being in all cases larger with the increase of hydrochloric acid.

From these experiments it is proved that titration with permanganate is far less reliable in the presence of free hydrochloric than of sulphuric acid, owing, undoubtedly, to the reaction previously explained. All researches, however, go to prove that when a solution of the substance to be titrated with hydrochloric acid is divided into three portions, and successively titrated in the same liquid, the mean of the second and third (setting the first entirely aside), will be trustworthy.

There can be very little doubt that the discrepancies shown to occur in the use of hydrochloric acid will account, in some measure, for the frequent want of accuracy in Pelouze's method for the determination of nitrates and similar processes. It is, therefore, advisable, in all possible cases, to use sulphuric acid for acidifying the solution and to avoid any large excess.

Where hydrochloric acid must be used and potassic bichromate is not admissible for titration, the fractional estimation beforementioned must be adopted, taking the second, or mean of the second and third titrations as correct; where this is not practicable it is best to prepare a mixture of hydrochloric acid and water, add some ferrous sulphate, and titrate with permanganate to the red tinge, then add the substance, and titrate with permanganate. Experiment has shown that this method is reliable.

TITRATION OF FERRIC SALTS BY PERMANGANATE.

§ 29. All ferric compounds requiring to be estimated by permanganate must of course be reduced to the ferrous state—this is best accomplished by metallic zinc in sulphuric acid solution—hydrochloric may also be used with due precaution (see § 28. 5).

The reduction may be accomplished by simply adding to the warm diluted solution small pieces of zinc, (free from iron, or at least with a known quantity present), until colourless, or until a drop of the solution brought in contact with a drop of potassic sulphocyanide produces no red colour.

The reduction may be hastened considerably either by using a flask containing so much amalgamated zinc in pieces (*i.e.*, zinc saturated with mercury) as to occupy almost as much space as the liquid, or by placing the liquid in a platinum crucible or basin, with small pieces of zinc; in this latter case a galvanic circuit is established, by which the reduction is accomplished with the use of very little zinc. The capsule should be covered with a glass plate or otherwise confined during the operation.

When the reduction is complete, no time should be lost in titrating the solution.

CALCULATION OF ANALYSES MADE WITH PERMANGANATE SOLUTION.

§ 30. THE calculation of analyses with permanganate, if the solution is not strictly decinormal, can be made by ascertaining its constant factor, reducing the number of c.c. used for it to decinormal strength, and multiplying the number of c.c. thus found by $\frac{1}{1000}$ of the equivalent weight of the substance sought; for instance—

Suppose that 15 c.c. of permanganate solution have been found to equal 0·1 gm. iron, it is required to reduce the 15 c.c. to decinormal strength, which would require 1000 c.c. of permanganate to every 5·6 gm. iron, therefore $5{\cdot}6 : 1000 :: 0{\cdot}1 : x =$ 17·85 c.c.; $17{\cdot}85 \times 0{\cdot}0056 = 0{\cdot}09996$ gm. iron, which is as near to 0·1 gm. as can be required. Or the factor necessary to reduce the number of c.c. used may be found as follows:—$0{\cdot}1 : 15 :: 5{\cdot}6 : x = 84$ c.c., therefore, $\frac{100}{84} = 1{\cdot}19$. Consequently 1·19 is the factor by which to reduce the number of c.c. of that special permanganate used in any analysis to the decinormal strength, from whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result:—

$$\begin{array}{ccccccc} \text{1 eq. Fe (56)} & & \text{eq. weight of} & & \text{the weight} & & \text{the weight of} \\ \text{or} & : & \text{the substance} & :: & \text{of Fe or} & : & \text{substance} \\ \text{1 eq. } \bar{O} \text{ (63)} & & \text{sought} & & \overset{\cdots}{O} \text{ found} & & \text{sought} \end{array}$$

In other words, if the equivalent weight of the substance analyse be divided by 56 or 63 (the respective equivalent weights of iron o oxalic acid), a factor is obtained by which to multiply the weigh of iron or oxalic acid, equal to the permanganate used, and th product is the weight of the substance analysed.

For example, copper is the substance sought, 1 eq. Cu. corresponding to 1 eq. Fe is 63·5, let this number therefore be divided by 56 $\frac{63·5}{56} = 1·134$, therefore, if the quantity of iron represente by the permanganate used in a copper analysis be multiplied b 1·134, the product will be the weight of the copper sought.

Again, in the case of manganic peroxide whose equivalent weigh is 43·5,

$$\frac{43·5}{56} = 0·7768,$$

the weight of iron therefore found by permanganate in any analysi multiplied by the factor 0·7768, will give the amount of mangani peroxide, MnO^2. Again, if m gm. iron $= k$ c.c. permanganate then, 1 c.c. permanganate $= \frac{m}{k}$ metallic iron.

Where possible the necessary factors will be given in the table preceding any leading substance.

CHROMIC ACID AND FERROUS OXIDE.

1. Potassic Bichromate.

$Cr^2K^2O^7 = 295$. Decinormal solution = 4·917 gm. per litre.

§ 31. This substance, which appears to have been first propose by Penny, possesses the advantage over permanganate, that i is absolutely permanent in solution, may frequently be obtaine in ordinary commerce in a pure state, and its solution ma be used in Mohr's burette without undergoing the chang peculiar to permanganate; on the other hand, the end of th reaction in the estimation of iron can only be known by an externa indicator, that is to say, a drop of the mixture is brought in contac with a drop of solution of red potassic-prussiate (freshly prepared upon a white slab or plate; while the ferrous oxide is in tolerable excess, a rich blue colour occurs at the point of contact between the drops, but as this excess continues to lessen by the addition of the bichromate, the blue becomes somewhat turbid, having first a green, then a grey, and lastly a brown shade. When the greenish blue tint has all disappeared, the process is finished. This series of changes in the colour admits of tolerably sure reading of the burette, after some little practice is obtained.

The reaction between chromic acid and ferrous oxide may be represented by the formula:—

$$2CrO^3 + 6FeO = Cr^2O^3 + 3Fe^2O^3.$$

The decomposition takes place immediately, and at ordinary temperatures, in the presence of free sulphuric or hydrochloric acid; nitric acid is of course inadmissible.

The reduction of ferric compounds to the ferrous state may be accomplished by zinc* or sulphurous acid as for permanganate; or, instead of these, stannous chloride may be used, which acts very rapidly as a reducing agent upon ferric oxide, the yellow colour of the solution disappearing almost immediately.

In the analysis of iron ores this method of reduction is serviceable; the greatest care, however, is necessary that the stannous chloride is not present in excess, as this would consume the bichromate solution equally with the ferrous oxide, and so lead to false results.

The discharge of the yellow colour of the iron solution may with care be made a very sure indication of the exact point of reduction. The concentrated hydrochloric solution of iron is heated to gentle boiling, and the moderately dilute tin solution added with a pipette, waiting a moment for each addition till the last traces of colour have disappeared; the solution is then poured into a beaker, diluted with water, and titrated with the bichromate as usual; an extra security is obtained by adding a few drops of potassic sulphocyanide to the solution, the disappearance of the blood-red colour indicating that no more ferric oxide is present.

In order to obviate the inaccuracy which would be produced by an excess of tin in the state of protosalt, Mohr recommends that chlorine water should be added by drops to the mixture until a rod moistened with it and brought in contact with blue iodide of starch paper no longer removes the colour, the excess of stannous chloride is then all converted into stannic chloride, and the titration with bichromate may proceed as usual.

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* When zinc is used, the zinc ferricyanide somewhat obscures the critical point in testing with the indicator.

It is absolutely necessary that the solution of potassic ferricyanide used as the indicator with bichromate, should be free from ferrocyanide; and as a solution when kept for some long time becomes in some measure converted into the latter, it is best to use a freshly-prepared liquid.

2. Preparation of the Decinormal Solution of Bichromate.

4·917 gm. per litre.

The reaction which takes place between potassic bichromate and ferrous oxide is as follows—

$$6FeO + Cr^2K^2O^7 = 3Fe^2O^3 + Cr^2O^3 + K^2O$$

It is therefore necessary that $\frac{1}{6}$th eq. in grammes should be used for the litre as a normal solution, and $\frac{1}{60}$th for the decinormal; and as it is preferable on many accounts to use a dilute solution, the latter is the most convenient for general purposes.

According to the latest and most reliable researches, the equivalent number of chromium is 52·5, and consequently that of potassic bichromate is 295; if, therefore, $\frac{1}{60}$th of this latter number = 4·917 gm. be dissolved in a litre of water, the decinormal solution is obtained. On the grain system, 49·17 grains to 10,000 grains of water will give the same solution.

1 c.c. of this solution is capable of yielding up $\frac{1}{10000}$ eq. in grammes of oxygen, and is therefore equivalent to the $\frac{1}{10000}$ eq. of any substance which takes up 1 equivalent of oxygen.

3. Solution of Stannous Chloride.

About 6 gm. pure tin in thin pieces (not the commercial tin-foil containing lead) is put into a large platinum capsule, and about 200 c.c. strong hydrochloric acid poured over it, and heated till it is dissolved; or it may be dissolved in a porcelain capsule or glass flask, adding pieces of platinum foil to excite a galvanic current. The solution so obtained is diluted to about a litre with pure fresh distilled water, and preserved in the bottle (fig. 17), or in any other well-closed vessel.

Its strength alters slightly from day to day, however well kept, and consequently it must be titrated for each day's use with $\frac{N}{10}$ iodine and starch, as described further on.

Examples of Analysis. 0·7 gm. of pure and dry double sulphate of iron and ammonia=0·1 gm. iron, was dissolved in about 2 oz. of water and titrated with decinormal bichromate, of which 17·85 c.c. were required; this multiplied by 0·0392 gave 0·699 gm. instead of 0·7 gm.

0·56 gm. of iron wire required 99·8 c.c.=0·5588 gm.; as it is impossible to obtain iron wire perfectly pure, the loss is undoubtedly owing to the impurities.

If the bichromate solution should from any accidental cause be found not strictly of decinormal strength, the factor necessary for converting it must be found as previously described.

As it is not at all an uncommon occurrence, in an analysis where no sign of the end of the reaction is visible in the solution itself, to overstep the exact point, it is advisable to have some method of bringing it into order again; this may be accomplished in the present case by adding a definite quantity of the double iron salt to the mixture, titrating afresh, and deducting the proportional amount of bichromate from the total quantity required.

IODINE AND SODIC HYPOSULPHITE.

§ 32. THE principle of this now beautiful and exact method of analysis was first discovered by Dupasquier, who used a solution of sulphurous acid instead of sodic hyposulphite. Bunsen improved his method considerably by ascertaining the sources of failure to which it was liable, which consisted in the use of a too concentrated solution of sulphurous acid; the reaction between iodine and very dilute sulphurous acid may be represented by the formula:—

$$SO^2+I^2+2H^2O=2HI+H^2SO^4.$$

If the sulphurous acid is more concentrated, *i.e.*, above 0·04 per cent., in a short time the action is reversed, the irregularity of decomposition varying with the quantity of water present, and the rapidity with which the iodine is added.[*] Under proper regulation, therefore, we see that free iodine converts sulphurous into sulphuric acid by decomposing water, the oxygen of which goes to the sulphurous, and produces sulphuric acid; the hydrogen being taken by the iodine, forming hydriodic acid.

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[*] This irregularity is now obviated by the use of sesquicarbonate of ammonia, or bicarbonate of soda. Mohr finds that either of these salts added in moderate quantity to the liquid sulphurous acid, or in the case of sulphites, dissolving them in the alkaline solution previous to titration with iodine, entirely overcomes the difficulty hitherto found in concentrated solutions.

There are great drawbacks, however, connected with the use of sulphurous acid; it very rapidly changes by keeping even in the most careful manner, so much so, that a sample tested in the morning would very frequently need an examination in the afternoon; and as it must be exceedingly dilute, it necessitates the use of special vessels and burettes. Taking all these things into account, therefore, the substitution of sodic hyposulphite is a great advantage, inasmuch as the end is secured quite as accurately without the trouble and insecurity connected with the sulphurous acid. The reaction in the case of sodic hyposulphite is as follows:—

$$2S^2O^3Na^2 + 2I = 2NaI + S^4O^6Na^2,$$

the result being that hyposulphurous acid takes oxygen from the water, with the production of tetrathionic and hydriodic acids in combination with soda.

In order to ascertain the end of the reaction in analysis by this method an indicator is necessary, and the most delicate and sensitive for the purpose is starch, which produces with the slightest trace of free iodine in cold solution the well-known blue iodide of starch. Hydriodic acid or iodides have no influence upon the colour.

The principle of this method, namely, the use of iodine as an indirect oxidising body by its action upon the elements of water, forming hydriodic acid with the hydrogen, and liberating the oxygen in an active state, can be applied to the determination of a great variety of substances with extreme accuracy.

Bodies which take up oxygen, and decolorise the iodine solution, such as sulphurous acid, sulphites, sulphuretted hydrogen, alkaline hyposulphites and arsenites, stannous chloride, &c., are brought into dilute solution, starch liquor added, and the iodine delivered in with constant shaking or stirring until a point occurs at which a final drop of iodine colours the whole blue—a sign that the substance can take up no more iodine, and that the drop in excess has shown its characteristic effect upon the starch.

Free chlorine, or its active compounds, cannot, however, be titrated with hyposulphite directly owing to the fact that, instead of tetrathionic acid being produced as with iodine, sulphuric acid occurs, as may be readily seen by testing with baric chloride. In such cases, therefore, the chlorine must be evolved from its compound and passed into an excess of solution of pure potassic iodide, where it at once liberates its equivalent of iodine, which can then, of course, be estimated with hyposulphite.

All bodies which contain available oxygen, and which evolve chlorine when boiled with strong hydrochloric acid, such as the chromates, manganates, and all metallic peroxides, can be readily and most accurately estimated by this method.

1. Preparation of the Decinormal Solution of Iodine.

I=127; 12·7 gm. per litre.

Chemically pure iodine may be obtained by mixing commercial iodine with about one-fourth of its weight of potassic iodide, and gently heating the mixture between two large watch-glasses or porcelain capsules, the lower one being placed upon a heated iron plate, the iodine sublimes in brilliant plates which are absolutely pure, the re-sublimed iodine of commerce is not always free from chlorine, it is therefore sometimes necessary to prepare it specially by a second sublimation as described above.

The watch-glass or capsule containing the iodine is placed under the exsiccator to cool, and also to deprive it of any traces of watery vapour; then 12·7 gm. are accurately weighed, and together with about 18 gm. of pure white potassic iodide dissolved in about 250 c.c. of water, and diluted to exactly one litre. The same solution may be obtained by dissolving 127 grains of iodine, and 180 of potassic iodide in 10,000 grains of water; in either case the solution is strictly decinormal; the flask must not be heated in order to promote solution, and care must be taken that iodine vapours are not lost in the operation.

The solution is best preserved in stoppered bottles of about 5 or 6 oz. capacity, which should be completely filled.

2. Decinormal Sodic Hyposulphite.

$Na^2S^2O^3,5H^2O=248$;=24·8 gm. per litre.

As it is not difficult either to manufacture or procure pure sodic hyposulphite, this quantity, powdered and dried between blotting paper, may be weighed directly, and dissolved in a litre of distilled water, and then titrated with the iodine solution and a little starch liquor; or the solution may be checked with $\frac{N}{10}$ bichromate as recommended by Mohr, by digesting an excess of bichromate, potassic iodide, and hydrochloric acid in the stoppered flask (fig. 25) or similar well closed vessel; when the mixture has cooled the liberated iodine is measured by the hyposulphite solution and its power ascertained. If impure hyposulphite should have been used, or the sample was not entirely free from accidental moisture, it will be necessary to find a factor by which to reduce it to decinormal strength, as described for previous solutions, or the amount of impurity being known, a fresh quantity may be prepared of proper strength. It is advisable to preserve the solution in the dark. After a time all solutions of hyposulphite undergo a slight amount of oxidation, and sulphur deposits upon the bottle, it is therefore always better to examine it previous to use. Mohr states that the tendency to deposit sulphur in the solution may be entirely obviated by adding to the $\frac{N}{10}$ solution, sesquicarbonate of ammonia in the proportion of 2 grammes to the litre, this does not in the least interfere with the colour produced with the starch indicator.

Beside the decinormal iodine and hyposulphite, it is convenient in some cases to use centinormal solutions, which can readily be prepared by diluting 100 c.c. of each decinormal solution to 1 litre.

In using the iodine solution, Mohr's burette may be employed, but care must be taken that the solution is not left in it for any length of time, as decomposition slowly takes place, and the tube becomes hard; Gay Lussac's, or the tap burette, are on this account preferable.

3. Starch Liquor.

1 part of clean arrowroot, potato, wheat, rice, sago, or other starch, is first mixed smoothly with cold water into a paste, and about 150 or 200 times its weight of boiling water poured over it, and allowed to stand and settle; the clear liquor only is to be used as the indicator, of which a few drops only are necessary. The liquor may be preserved from decomposition for some time by adding to it about one per cent of salicylic acid in crystal, this, however, is not so sensitive as the freshly prepared solution.

Example of Titration: A crystal of pure sodic hyposulphite weighing 0·634 gm. was dissolved in distilled water, starch added, and 27·2 c.c. of iodine solution of unknown strength required to produce the blue colour, since the $\frac{N}{10}$ hyposulphite should contain 24·8 gm. per litre, the quantity of iodine solution, if rigidly decinormal, should be

$$24{\cdot}8 : 1000 :: 0{\cdot}634 : x = 25{\cdot}56 \text{ c.c.};$$

but the quantity actually used was 27·2 c.c.; the coefficient therefore is

$$\frac{25{\cdot}56}{27{\cdot}2}=0{\cdot}94.$$

Bichromate solution being very permanent, it is an exact and convenient agent for titrating the strength of a hyposulphite solution as follows:—

Let a convenient quantity, say 20 c.c. of bichromate be measured into a stoppered flask, adding solution of pure potassic iodide in sufficient excess to keep the liberated iodine in solution, then add about 5 c.c. of hydrochloric acid, heat on the water-bath, and shake together for a few minutes until the decomposition is complete, when cold add starch, and titrate with hyposulphite until colourless, the number of c.c. of bichromate divided by that of the hyposulphite will give the coefficient necessary for correcting the hyposulphite to $\frac{N}{10}$ strength.

ANALYSIS OF SUBSTANCES BY DISTILLATION WITH HYDROCHLORIC ACID.

§ 33. There are a great variety of substances containing oxygen, which when boiled with hydrochloric acid, yield chlorine, equivalent to the whole or a part only of the oxygen they contain according to circumstances. Upon this fact are based the variety of analyses which may be accomplished by means of iodine and sodic hyposulphite; the chlorine so evolved, however, is not itself estimated, but is conveyed by means of a suitable apparatus into a solution of potassic iodide, thereby liberating an equivalent quantity of iodine. This latter body is then estimated by hyposulphite; the quantity so found is, therefore, a measure of the oxygen existing in the original substance, and consequently a measure of the substance itself. It seems a very roundabout method, and one would imagine it could scarcely lead to accurate results; nevertheless, without exaggeration, it may be said to be the most exact in the whole range of volumetric analysis, far outstripping any process of analysis by weight.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkaline iodide, may possess a variety of forms,—the most serviceable, however, being the three kinds devised respectively by Bunsen, Fresenius, and Mohr.

Bunsen's consists of a small flask to contain the mixture for distillation, connected by a stout piece of vulcanized tubing with a long bent tube, which is carried into the solution of iodide contained in an inverted retort, the neck of the latter having a tolerably large bulb blown midway, so that when the chlo all evolved from the mixture, and hydrochloric acid gas be distil, the rapid condensation which ensues may not cau liquid to rush back to the flask; and so spoil the ope This regurgitation is a great nuisance, and in order to the entrance of the liquid into the bent tube, Bunse trived a little self-acting valve, which consists of a very glass bulb with a stalk (very like the large headed ornament used by ladies for their hair); this presents no hindrance evolution of the gas during the distillation, but when the attempts to enter, the bulb is forced up to the end of the d tube, so as to close the entrance; a drawing of the entire ap may be seen in most treatises on chemical analysis.

A far better preventive of this regurgitation is, however, su by Freseni applicable t kind of ap —namely, t dition of pieces of magnesite magnesic ate); this su dissolves bu in the hydr acid, and s up a consta of carboni gas, whose is sufficient vent the re the liquid.

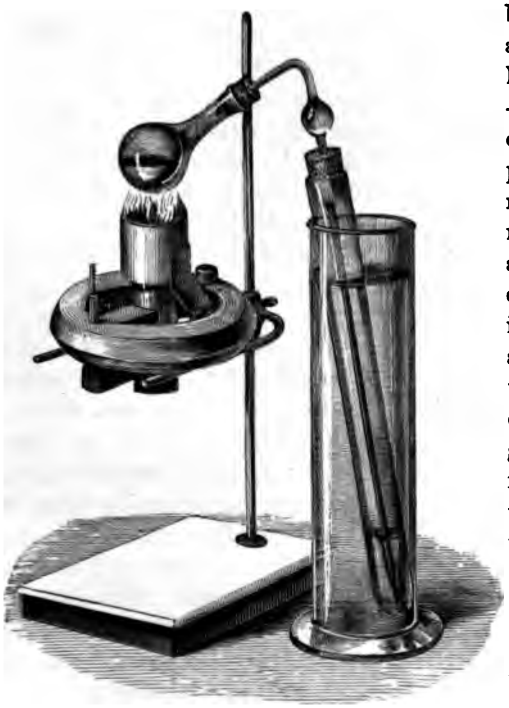

Fig. 23.

The ap contrived Fresenius from Bu only in hav large bulbs in the neck of the retort, and one in the bent delivery tub

Mohr's apparatus is shown in fig. 23, and is, on accoun simplicity of construction, very easy to use.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffin; through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely in a stout tube about 12 or 13 inches long and 1 inch wide, closed at one end like a test tube; this tube containing the alkaline iodide, is placed in an ordinary hydrometer glass, about twelve inches high, and surrounded by cold water; the delivery tube is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the tall hydrometer glass keeps everything in position. The substance to be distilled is put into the flask and covered with strong hydrochloric acid, the magnesite added, the condenser supplied with a sufficient quantity of iodide solution, and the apparatus put together tightly; either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at pleasure; in the case of the common spirit lamp, it may be held in the hand, and applied or withdrawn according to the necessities of the case; the argand spirit or gas lamp can, of course, be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved, should be more than will remain in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask, and preserved for analysis, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner previously described.

Instead of the large test tube, some operators use a U tube to contain the potassic iodide, having a bulb in each limb, but the latter is not necessary if magnesite is used.

The solution of potassic iodide may conveniently be made of such a strength that $\frac{2}{10}$ eq. or 33·2 gm. is contained in the litre. One cubic centimeter will then be sufficient to absorb the quantity of free iodine, representing 1 per cent. of oxygen in the substance analysed, supposing it to be weighed in the metric system. In examining peroxide of manganese, for instance, 0·436 gm. or 4·36 grn. would be used, and supposing the percentage of peroxide to be about sixty, 60 c.c. or dm. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 c.c. or dm. should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine. It may sometimes happen that not enough iodide is present to keep all the liberated iodine in solution —in which case it will separate out in the solid form; more iodide, however, may be added to dissolve the iodine; the titration can then be made as usual.

The process of distillation above described may be avoided in many cases. There are a great number of substances which, by mere digestion with hydrochloric acid and potassic iodide at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to regrind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water, if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 1 to 5 or 6 oz., according to the necessities of the case.

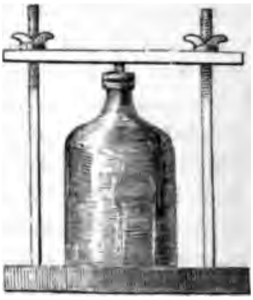

Fig. 24.

The stopper may be secured by fine copper binding wire, or a kind of clamp contrived by Mohr may be used, as shown in fig. 24; by means of the thumb screws the pressure upon the stopper may be increased to almost any extent.

The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of potassic iodide and pure hydrochloric acid added; the stopper is then inserted, fastened down, and the bottle suspended in a water bath, and the water is gradually heated to boiling by a gas flame or hot plate as may be most convenient; when the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and after being shaken, emptied into a beaker, and the liquid diluted by the washings for titration.

The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation. Many of them even at ordinary temperatures.

The potassic iodide used in the various analyses must be absolutely free from potassic iodate and free iodine.

ARSENIOUS ACID AND IODINE.

§ 34. The principle upon which this method of analysis is based is the fact, that when arsenious acid is brought in contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being —

$$As^2O^3 + 4I + 2Na^2O = As^2O^5 + 4NaI.$$

The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of carbonate, as caustic alkalies interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of sodic carbonate, the blue colour does not occur until all the arsenious acid is oxidised into arsenic acid; in like manner, a standard solution of arsenious acid may be used for the estimation of iodine or other bodies which possess the power of oxidising it.

The chief value, however, of this method is found in the estimation of free chlorine existing in the so-called chloride of lime, chlorine water, hypochlorites of lime, soda, &c., in solution; generally included under the term of chlorimetry.

1. Preparation of the Decinormal Solution of Sodic Arsenite.

$$As^2O^3 = 198; \ 4{\cdot}95 \text{ gm. per litre.}$$

The iodine solution is the same as described in § 32, containing 12·7 gm. per litre.

The corresponding solution of sodic arsenite is prepared by dissolving 4·95 gm. of the purest sublimed arsenious anhydride free from sulphide, in about 250 c.c. of distilled water in a flask, with about 25 gm. of the purest crystallised sodic monocarbonate, free from sulphide, hyposulphite, or sulphite. It is necessary that the acid should be in powder, and the mixture needs boiling a shaking for some time in order to complete the solution; wh this is accomplished the mixture is diluted somewhat, then ma up to the litre.

In order to test this solution, 10 c.c. are put into a beaker w a little starch liquor, and the iodine solution allowed to flow in fror burette, graduated in $\frac{1}{10}$ c.c. until the blue colour appears, if exac 10 c.c. are required the solution is strictly decinormal, if otherwi the necessary factor must be found for converting it to that streng

Starch liquor, however, cannot be used for the direct estimati of free chlorine, consequently resort must be had to an exter indicator, and this is very conveniently found in iodide of star paper, which is best prepared by mixing a portion of starch liqu with a few drops of solution of potassic iodide on a plate, a soaking strips of pure filtering paper therein; the paper so prepar is used in the damp state, and is far more sensitive than dried paper prepared according to Penot's plan.

2. The Analytical Process.

In all cases the chlorine to be estimated must exist in an alkal solution. In the case of chloride of lime this is already acco plished by the caustic lime which invariably exists in the compou

The substance being brought under the burette containing arsenious acid solution, the latter is suffered to flow until a drop the mixture taken out with a glass rod and brought in contact w the prepared paper, no longer produces a blue spot. As the col becomes gradually lighter towards the end of the process, it is difficult to hit the exact point; should it, however, by any accid be overstepped, starch liquor may be added to the mixture, a decinormal iodine solution added until the blue colour is produc the quantity so used is then deducted from the total arsenic soluti

Examples: 50 c.c. of chlorine water were mixed with solut of sodic carbonate, and brought under the arsenic burette, and c.c. of solution added; on touching the prepared paper with mixture no colour was produced, consequently the quantity u was too great; starch liquor was therefore added and decinor iodine, of which 3·2 c.c. were required to produce the blue colo This gave 16·8 c.c. of arsenic solution, which multiplied by 0·003 gave 0·05964 gm. of Cl in the 50 c.c. A second operation with same water required 16·8 c.c. of arsenic solution direct, before end of the reaction with iodised starch paper was reached.

The arsenic solution is equally as serviceable as hyposulphite the general estimation of iodine, sulphuretted hydrogen, chroma &c., by distillation with hydrochloric acid.

PART IV.

ANALYSIS BY PRECIPITATION.

INTRODUCTION.

§ 35. The general principle of this method of determining the quantity of any given substance is alluded to in § 1, and in all instances is such that the body to be estimated forms an insoluble precipitate with a titrated reagent. The end of the reaction is, however, determined in three ways.

1. By adding the reagent until no further precipitate occurs, as in the determination of chlorine by silver.

2. By adding the reagent in the presence of an indicator contained either in the liquid itself, or brought externally in contact with it, so that the slightest excess of the reagent shall produce a characteristic reaction with the indicator, as in the estimation of silver with salt by the aid of potassic chromate, or that of phosphoric acid with uranium by yellow potassic prussiate.

3. By adding the reagent to a clear solution until a precipitate occurs, as in the estimation of cyanogen by silver.

The first of these endings can only be applied with great accuracy to silver and chlorine estimations. Very few precipitates have the peculiar quality of chloride of silver, namely, almost perfect insolubility, and the tendency to curdle closely by shaking, so as to leave the menstruum clear; some of the most insoluble precipitates, such as baric sulphate and calcic oxalate, are unfortunately excluded from this class, because their finely-divided or powdery nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two processes, viz., the determination of cyanogen by silver, and that of chlorides by mercuric nitrate.

Since the estimation of chlorine or hydrochloric acid by precipitation with silver can be used in many cases for the indirect estimation of many other substances with great exactness, the preparation of the necessary standard solutions will now be described.

1. Preparation of the Decinormal Solution of Silver.

17 gm. $AgNO^3$ per litre.

10·8 gm. of pure silver are dissolved in pure dilute nitric acid with gentle heat in a flask, into the neck of which a small funnel is dropped to prevent loss of liquid by spirting; when solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to 1 litre; or if it be desired to use potassic chromate as indicator in any analysis, the solution must be neutral; in which case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in 1 litre; or, what is preferable, 17 gm. of pure and dry recrystallised nitrate of silver are dissolved in one litre of distilled water. If the grain system is used, 108 grn. of silver or 170 grn. of nitrate are dissolved, and the solution diluted to 10,000 grains.

1 c.c. of this solution = 0·0108 gm. Ag. or
0·017 „ $Ag.NO^3$.

2. Preparation of the Decinormal Solution of Salt.

5·85 gm. NaCl per litre.

5·85 gm. of pure sodic chloride are dissolved in distilled water, and the solution made up to 1 litre, or 58·5 grn. to 10,000 grains.

There are two methods by which the analysis may be ended—

a. By adding silver cautiously, and well shaking after each addition till no further precipitate is produced.

b. By using a few drops of solution of potassic chromate as indicator, as devised by Mohr.

For the ending *a* refer to § 36. 1.

The ending *b* is exceedingly serviceable, on the score of saving both time and trouble. There are conditions, however, attached to its use, which must not be disregarded. The most important of these is, that the solutions must be absolutely free from acid or any great excess of alkali; it is best to have them neutral. When, therefore, acid is present in any solution to be examined, it should be neutralised with sodic carbonate in very slight excess.

CHLORINE.

Cl. = 35·5.

1 c.c. or 1 dm. $\frac{N}{10}$ silver solution = 0·00355 gm. or 0·0355 grn. of Chlorine.
" " " = 0·00585 gm. or 0·0585 grn. of Sodic chloride.

§ 36. **The** powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the assay of silver by the wet method of Gay Lussac. The details of the process are more particularly described under the article relating to the assay of silver; the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic, and for exactness and convenient dilution are of decinormal strength. In many cases it is advisable to possess also centinormal solutions, made by diluting 100 c.c. $\frac{N}{10}$ solution to 1 litre.

1. The Analytical Process by Direct Precipitation.

Very weak solutions of chlorides, such as drinking waters, are not easily examined for chlorine by direct precipitation, unless they are considerably concentrated by evaporation previous to treatment, owing to the fact that, unless a tolerable quantity of chloride can be formed, it will not collect together and separate so as to leave the liquid clear enough to tell on the addition of fresh silver whether a distinct formation of chloride occurs. The best effects are produced when the mixture contains chlorine equal to from 1½ to 2 gm. of salt per 100 c.c. Should the proportion be much less than this, the difficulty of precipitation may be overcome by adding a quantity of freshly precipitated chloride, made by mixing equal volumes of $\frac{N}{10}$ salt and silver solution, shaking vigorously, pouring off the clear liquid, and adding the chloride to the mixture under titration. The best vessel to use for the trial is a well-stoppered round white bottle, holding 100 to 150 c.c. and fitting into a paper case, so as to prevent access of strong light during the analysis. Supposing, for instance, a neutral solution of potassic chloride requires titration, 20 or 30 c.c. are measured into the shaking bottle, a few drops of strong nitric acid added (free acid must always be present in direct precipitation,) and a round number of c.c. of silver solution added from the burette. The bottle is placed in its case, or may be enveloped in a dark cloth and vigorously shaken for half a minute, then uncovered, and gently tapped upon a table or book, so as to start the chloride downward from the surface of the liquid where it often swims; a quick clarification indicates excess of silver; the nearer the point of exact counterbalance the more difficult to obtain a clear solution by shaking, but a little practice soon accustoms the eye to distinguish the faintest precipitate.

In case of overstepping the balance in any trial, it is only necessary to add to the liquid under titration a definite volume of $\frac{N}{10}$ salt solution, and finish the titration in the same liquid—deducting, of course, the same number of c.c. of silver as have been added of salt solution.

Fuller details and precautions are given in the section on silver assay, to which the reader should refer.

2. The Analytical Process, with Potassic Chromate as Indicator, specially applicable to Waters and Weak Solutions of Chlorides.

To the neutral or faintly alkaline solution, two or three drops of a cold saturated solution of yellow potassic chromate are added, and the silver solution delivered from the burette until the last drop or two produce a faint blood-red tinge, an evidence that all the chlorine has entered into combination with the silver, and the slight excess has formed a precipitate of chromate of silver; the reaction is very delicate and easily distinguished.

Example: 1 gm. of pure sodic chloride was dissolved in 100 c.c. of water, a few drops of chromate solution added, and titrated with $\frac{N}{10}$ silver, of which 17·1 c.c. were required to produce the red colour; multiplied by the $\frac{N}{10}$ factor for sodic chloride=0·00585, the result was 1·00035 gm. NaCl, instead of 1 gm.

INDIRECT ESTIMATION OF AMMONIA, SODA, POTASH, LIME, AND OTHER ALKALIES AND ALKALINE EARTHS, WITH THEIR CARBONATES, NITRATES, AND CHLORATES, ALSO NITROGEN, &c., BY MEANS OF DECINORMAL SILVER SOLUTION, AND POTASSIC CHROMATE, AS INDICATOR.

1 c.c. $\frac{N}{10}$ silver solution = $\frac{1}{10000}$ H eq. of each substance.

§ 37. MOHR, with his characteristic ingenuity, has made use of the delicate reaction between chlorine and silver, with potassic chromate as indicator, for the determination of the bodies mentioned above. All compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid may be determined with great accuracy. The chlorine in a combined state is, of course, the only substance actually determined, but as the laws of chemical combination are exact and well known, the measure of chlorine is also the measure of the base with which it is combined.

In most cases it is only necessary to slightly supersaturate the alkali, or its carbonate, with pure hydrochloric acid; evaporate on the water bath to dryness, and heat for a time to 120° C. in the air bath, then dissolve to a given measure, and take a portion for titration.

Alkalies and Alkaline Earths with organic acids are ignited to convert them into carbonates, then treated with hydrochloric acid, and evaporated as before.

Carbonic Acid in combination may be determined by precipitation with baric chloride, as in § 24; the washed precipitate is dissolved on the filter with hydrochloric acid, (covering it with a watch-glass to prevent loss,) and then evaporated to dryness. In order to titrate with accuracy by the help of potassic chromate, the baryta must be precipitated by means of a solution of pure sodic or potassic sulphate, added in slight excess; the precipitated baric sulphate does not interfere with the delicacy of the reaction; if this precaution were not taken, the yellow baric chromate would mislead.

Free Carbonic Acid is collected by means of ammonia and baric chloride, as in § 24, and the estimation completed as in the case of combined CO^2.

Chlorates are converted into chlorides by ignition, then titrated with $\frac{N}{10}$ silver and chromate.

Nitrates are evaporated with concentrated hydrochloric aci and the resulting chlorides titrated, as in the previous case.

Nitrogen. The ammonia evolved from guano, manures, oi cakes, and sundry other substances, when burned with soda lin in Will and Varrentrapp's apparatus, is conducted throug dilute hydrochloric acid; the liquid is carefully evaporated to dr ness, before titration.

In all cases the operator will, of course, take care that no chlori from extraneous sources but the hydrochloric acid is present, or it exists in the bodies themselves as an impurity, its quantity mu be first determined.

Example: 0·25 gm. pure sodic carbonate was dissolved in wate and hydrochloric acid added till in excess; it was then dried on t water-bath till no further vapours of acid were evolved; the resulti white mass was heated for a few minutes to about 120° C., di solved and made up to 300 c.c.; 100 c.c. required 15·7 c.c. silver, this multiplied by 3 gave 47·1 c.c., which multiplied by t $\frac{N}{10}$ factor for sodic carbonate = 0·0053, gave 0·24963 gm. inste of 0·25 gm.

Indirect Estimation of Potash and Soda existing Mixed Chlorides.

It is a problem of frequent occurrence to determine the relati quantities of potash and soda existing in mixtures of the tw alkalies—such as occur, for instance, in urine, manures, soi waters, &c. The actual separation of potash from soda by mea of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenie since a careful estimation of the chlorine present in the mixture the only labour required, and this can most readily be accor plished by $\frac{N}{10}$ silver and potassic chromate, as previously describe

1. The weight of the mixed pure chlorides is accurately fou and noted.
2. The chlorides are then dissolved in water, and very careful titrated with $\frac{N}{10}$ silver and chromate for the amount of chlori present, which is also recorded; the calculation is then follows:—

The weight of chlorine is multiplied by the factor 2·1029; fro the product so obtained is deducted the weight of the mixed sal found in 1. The remainder multiplied by 0·36288 will give t weight of sodic chloride present in the mixture.

The weight of sodic chloride deducted from the total as found 1 will give the weight of potassic chloride.

Sodic chloride × 0·5302 = Soda (Na^2O).
Potassic chloride × 0·6317 = Potash (K^2O).

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis. It is necessary, however, to bear in mind that this method of calculation can only be relied on when the two bases exist in about equal quantities, or at least not less than one part of one to two of the other.

Another method of approximately estimating the proportion of soda and potash existing as mixed chlorides is given by Anthon, (Dingler's Polytech. Journ., 1871, 286,) as follows :—

The mixed pure chlorides are rendered perfectly dry, 2·71 gm. weighed, dissolved in water, and the solution made up to 100 c.c.; 10 c.c. of this solution are then titrated with $\frac{N}{10}$ silver and chromate. The proportion of Na Cl is found by the following table :—

C.C. $\frac{N}{10}$ silver used.		Percentage of Na Cl.	C.C. $\frac{N}{10}$ silver used.		Percentage of Na Cl.
36·3	=	0	39·3	=	30
36·4	=	1	39·8	=	35
36·5	=	2	40·3	=	40
36·6	=	3	40·8	=	45
36·7	=	4	41·3	=	50
36·8	=	5	41·8	=	55
37·3	=	10	42·3	=	60
37·8	=	15	42·8	=	65
38·3	=	20	43·3	=	70
38·8	=	25	43·8	=	75

Since $\frac{1}{10}$ c.c. represents 1% Na Cl, this method can hardly be relied upon where great accuracy is required.

PART V.

APPLICATION OF THE FOREGOING PRINCIPLES OF ANALYSIS TO SPECIAL SUBSTANCES.

SODA.

1. Soda Ash, Black Ash; Mother Liquors, &c.

§ 38. In refined alkali, moisture is determined by heating 5 or 10 gm. to dull redness for ten minutes, in a small crucible of platinum, silver, iron, or porcelain, and allowing it to cool under a bell glass in the presence of sulphuric acid or calcic chloride; the difference between the first and second weighings is the accidental moisture in the sample.

The contents of the crucible are then dissolved in about 150 c.c. of warm distilled water, and any insoluble matter filtered off by a small filter, washed on the latter a few times with hot water, then, if necessary, dried, ignited, and weighed as insoluble matter. It is important that this insoluble matter be removed before titration, otherwise the lime and other constituents in it will consume a portion of the normal acid, and so register a higher percentage of alkali than is really present.

The total quantity of alkali is determined in a measured portion of the filtrate and washings, previously diluted to ½ or 1 litre, by normal sulphuric, nitric or oxalic acid, as in § 16.*

The quantity of caustic alkali present in any sample is determined as in § 16.

A custom prevails in the soda trade of calculating the atomic weight of sodium as 24 instead of 23, thus representing more real soda present in a sample of alkali than actually exists; this practically leads to an error of from 1 to 2 per cent. in a 50 per cent. ash, according to the method of calculation. This anomaly ought to be got rid of, and one uniform standard adopted.

The presence of sulphides is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated with an acid, or by dipping paper, steeped in sodic nitro-prusside, into the solution; if the paper turns blue or violet, sulphide is present.

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* This gives a slight error, owing to traces of aluminate of soda and lime, which consume acid.

The quantity of sulphide and hyposulphite may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch liquor, and titrating with decinormal iodine solution till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and hyposulphurous acid present. The quantity of each may be known by adding a solution of sulphate of zinc to a like quantity of the alkali, and filtering so as to remove the free carbonated and sulphuretted alkali, by which means the hyposulphurous acid alone remains, which may be estimated with iodine and starch as before; the quantity of iodine solution so required is to be deducted from the total, and the calculation for both sulphide and hyposulphite of sodium may then be made, 1 c.c. $\frac{N}{10}$ iodine is equal to 0·0248 gm. hyposulphite, or 0·0039 gm. sodic sulphide; good English alkali is seldom contaminated with these substances to any extent.

Sodic chloride (common salt) may be determined by neutralising 0·585 gm. or 5·85 grn. of the alkali with nitric acid, and titrating with decinormal silver solution and potassic chromate. Each c.c. or dm. corresponds to 1 per cent. of common salt, if the above weight is taken. Since the quantity of acid necessary to neutralize the alkali has already been found, the proper measure of $\frac{N}{10}$ nitric acid may at once be added.

Sodic sulphate is determined, either directly or indirectly, as in 40 § 4[illegible]; each c.c. or dm. of normal baric chloride is equal to 0·071 gm., or 0·71 grn. of dry sodic sulphate.

Black ash and raw mother liquors and lyes can be examined in precisely the same way as above; if oxide of iron is present it may be determined as in § 29; lime, by boiling with sodic carbonate and precipitation as carbonate—washing the precipitate thoroughly with boiling water, and titrating with normal acid and alkali, as in § 20.

Mohr gives the following as a specimen of analysis of soda liquor volumetrically:—

(1.) Sp. gr. 1·252.

(2.) 10 c.c. evaporated to dryness left after slight ignition 3·11 gm. = 311 gm. per litre.

(3.) Residue of 2 titrated with normal nitric acid required 56·2 c.c.; this includes the sodic sulphides.

(4.) 10 c.c. raw liquor neutralised with acetic acid required 6·82 c.c. $\frac{N}{10}$ iodine.

(5.) 10 c.c. precipitated with zinc sulphate to remove sulphide and the filtrate titrated with $\frac{N}{10}$ iodine required 2·44 c.c.

(6.) 10 c.c. raw liquor nearly neutralised with acetic acid and titrated for chlorine with $\frac{N}{10}$ silver and chromate required 11·4 c.c.

(7.) 10 c.c. raw liquor saturated with hydrochloric acid and titrated for sulphuric acid required 0·4 c.c. normal baric chloride.

The composition of the liquor was therefore as follows :—

(From 5.) The molecular weight of anhydrous sodic hyposulphite is 158, 1 c.c. $\frac{N}{10}$ iodine = 0·0158 gm. 2·44 c c. were required, therefore = 0·0385 gm. hyposulphite.

(From 4.) The 2·44 c.c. iodine required in 5 deducted from the 6·82 c.c. in 4, leaves 4·38 c.c. to represent the sodic sulphide—1 c.c. $\frac{N}{10}$ iodine = 0·0039 gm. sulphide, therefore 4·38 c.c. = 0·01708 gm.

(From 3.) The 4·38 c.c. iodine from 4 deducted from 56·2 c.c. normal acid leaves 55·76 c.c. which multiplied by the factor for sodic carbonate 0·053 gives 2·955 gm.

(From 6.) 11·4 c.c. $\frac{N}{10}$ silver × $\frac{N}{10}$ factor for salt 0·00585 = 0·0669 gm.

Hence the results may be tabulated as follows :—

Sodic carbonate	2·9550 gm.
„ chloride	0·0669 „
„ sulphite	0·0284 „
„ hyposulphite	0·0385 „
„ sulphide	0·0170 „
	3·1058
By evaporation	3·1100

In cases where an analysis of the total contents of a sample of black ash is required, the following method gives reliable results tolerably speedily. Most of the modes of determination are likewise applicable to samples of dry vat-waste :—(Wright*)

(*a*.) A known weight is dissolved in hydrochloric acid, the insoluble coke and sand collected on a weighed filter, and the carbon subsequently burnt off.

(*b*.) In the filtrate from (*a*) the H^2SO^4 is estimated by normal baric chloride.

(*c*.) A known weight is dissolved in nitric acid, and the Cl determined volumetrically by standard silver solution, or neutralised and titrated by the chromate method.

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* Chem. News, vol. xvi. p. 151.

(*d.*) A known weight is titrated in Mohr's CO^2 apparatus, fig. 20, the ammonic carbonate boiled with calcium chloride; the precipitate washed till the washings are neutral, dissolved in a slight excess of standard hydrochloric acid, and the excess determined by a standard alkaline solution; thus the CO^2 can be calculated.

(*e.*) A known weight is fused with four times its weight of a mixture of three parts dry sodium carbonate and one of potassium nitrate (both free from sulphate). From the total sulphate thus formed, and estimated volumetrically by barium, that existing as Na^2SO^4 is subtracted, and the remainder calculated as S.

(*f.*) A known weight is treated with hydrochloric acid, the filtrate oxidised by nitric acid, and the mixed Fe^2O^3, Al^2O^3 and P^2O^5 precipitated by ammonia.

(*g.*) The filtrate from *(f)* is treated with ammonic oxalate, the precipitate estimated volumetrically by permanganate, or gravimetrically as $CaCO^3$; hence the Ca is known.

(*h.*) A known weight is lixiviated with warm water, and in the filtrate from the insoluble matter the SiO^3 estimated by evaporation to dryness with hydrochloric acid; in the filtrate from this the Al^2O^4 combined as aluminate is determined by precipitating the alumina by ammonia.

(*i.*) A known weight is cautiously treated with sulphuric acid in a capacious platinum crucible, and heated till gases cease to be evolved; the residue is treated with water, filtered and well washed, ammonia and ammonium oxalate added to the filtrate; and ultimately the total Na contained weighed as Na^2SO^4.

In calculating results from the foregoing data, the Cl found is calculated as NaCl, the SO^3 as Na^2SO^4, the SiO^3 as Na^2SiO^3, and the Al^2O^4 (soluble in water) as $Na^2Al^2O^4$; the remaining sodium is then calculated as Na^2CO^3, and the remaining CO^2 as $CaCO^3$ The sulphur is calculated as CaS, and the remaining calcium as CaO. From the total $Al^2O^3 + Fe^2O^3 + P^2O^5$ the alumina present as aluminate is subtracted; the coke and sand, &c., are directly determined (*a.*) The difference from 100 in a carefully conducted analysis will not amount to more than a few tenths per cent, and represents cyanogen, traces of moisture, &c., and loss.

In an over-roasted ash the alkaline sulphide can only be safely estimated by digestion with nearly absolute alcohol, oxidation to sulphate by chlorine, and precipitation by barium. The Na contained as poly- or mono-sulphide, may be determined volumetrically by test acid in the alcoholic solution, and must be subtracted from that to be calculated as Na^2CO^3 as above: the S existing as poly- or mono-sulphide of sodium must be subtracted from the total sulphur found, the difference being calculated as CaS. (For further information see Wright, Chem. Soc. Journ. XX, 407.)

2. Estimation of mixed Caustic Soda and Potash.

(Dale, Watt's Dict. vol. i, p. 119.)

This process depends upon the fact that potassic bitartrate is almost insoluble in a solution of sodic bitartrate.

Add to the solution containing the mixed salts, a standard solution of tartaric acid till neutral or faintly acid—this produces neutral tartrates of the alkalies—now add the same volume of standard tartaric acid as before—they are now acid tartrates, and the potassic bitartrate separates almost completely, filter off the sodic bitartrate and titrate the filtrate with normal caustic soda; the quantity required equals the soda, originally in the mixture—the quantity of tartaric acid required to form bitartrate with the soda subtracted from the total quantity added to the mixture of the two alkalies, gives the quantity required to form potassic bitartrate, and thus the quantity of potash is found.

This process is only applicable for technical purposes.

3. Salt Cake

Is the impure sodic sulphate left in the retorts in preparing hydrochloric acid from sulphuric acid and salt, or nitric acid from sodic nitrate. It generally contains free sulphuric acid existing as sodic bisulphate, the quantity of which may be ascertained by direct titration with normal alkali.

The common salt present is estimated by decinormal silver solution and chromate; having first saturated the free acid with pure sodic carbonate, 1 c.c. or 1 dm. silver solution is equal to 0·00585 gm. or 0·0585 grn. of salt.

Sulphuric acid, combined with soda, is estimated either directly or indirectly as in § 40; 1 c.c. or 1 dm. of normal baryta solution is equal to 0·071 gm., or 0·71 grn. of dry sodic sulphate.

Iron is precipitated from a filtered solution of the salt cake with ammonia in excess, the precipitate of ferric oxide re-dissolved in sulphuric acid, reduced to the ferrous state with zinc and titrated with permanganate, as in § 29.

4. Raw Salt, Brine, &c.

Lime may be estimated by precipitation with ammonic oxalate, and the precipitate titrated with permanganate, as in § 49.

Sulphuric acid as in § 40.

Magnesia is precipitated as ammoniacal phosphate, by a solution of sodic phosphate containing ammonia, first removing the lime by ammonic oxalate, the precipitate of double phosphate of magnesia and ammonia is brought on a filter, washed with cold water containing ammonia, then dissolved in acetic acid, and titrated with standard uranium solution; each c.c. of solution required represents 0·0563 gm. magnesia; or the precipitate may be dried, ignited, and weighed as magnesic pyrophosphate.

The quantity of real salt in the sample may be ascertained by treating a weighed quantity in solution with caustic baryta, boiling, setting aside that the excess of baryta may precipitate itself as carbonate, or more quickly by adding ammonic carbonate, filtering, evaporating the solution to dryness, and gently igniting—the residue is pure salt. The loss of weight between this and the original specimen taken for analysis, will show the percentage of impurities.

5. Soap.

The only volumetric method that appears worth anything in the examination of commercial soaps, is based upon the principle of Clark's soap test for estimating the hardness of water. A standard soap is first chosen by means of which the relative saponifying power of any other soap may be ascertained.

Mottled Marseilles soap, generally known as Castile soap, may be taken as such a standard. This soap contains 30 per cent. of water, and is free from all mineral adulteration; its composition is, in round numbers,

Soda	6
Fatty acids	64
Water	30
	100

1 gm. of this soap will be exactly neutralised by 0·1074 gm. pure calcic chloride, or 10 grains by 1·074 grn.

Therefore a solution of 1·074 gm. $CaCl^2$ in a litre of water, or

10·74 grn. in 1000 dm. will suffice to neutralise respectively 10 g or 100 grn. of standard soap dissolved in the same volume of wat or rather alcohol and water.

The smallest excess of soap solution will give a persistent fro as in Clark's test.

Pons (Journ. de Ph. et Chem. Ap. 1865, p. 290,) applies t process as follows:—10 c.c. of the standard calcic solution a placed in a stoppered bottle holding 70—100 c.c. with about 20 c. distilled water; 10 gm. soap are then dissolved in 100 c.c. alcoh ·825 sp. gr., by means of rubbing or shaking with gentle heat—t real soap dissolves and leaves all mineral or foreign matters, whi may be filtered off, and afterwards examined if necessary; t filtered soap solution is now diluted to one litre with distilled wat and a burette filled with it ready to add to the lime solution in t shaking bottles. It is then cautiously run into the lime wi frequent shaking until a lather is obtained; the 10 c.c. of li solution divided by the number of c.c. of soap solution require will show the richness of the soap as compared with the standa —if 10 c.c. only are used, the soap under examination is of t same quality as the standard; if 15 or 20 c.c. are required, t percentage will be $\frac{10}{15} = 66\%$ or $\frac{10}{20} = 50\%$, and so on.

The alkali may be determined by igniting a weighed quantity the dry soap, and titrating with normal acid—if salt is present may be estimated in the ash by $\frac{N}{10}$ silver and chromate.

POTASH.

1. Raw Caustic Potash, Pearlash, Kainite, &c.

§ 39. The examination of raw potash salts and mother liquo where the alkali exists free or as carbonate, is conducted precise in the same way as has already been described in the case of sod

In cases, however, where potash exists in combination as neutral salt, such as kainite or kieserite, &c., or as a constituent minerals, it has to be first separated as double chloride of potassiu and platinum. The method usually adopted is that of collecti the double salt upon a tared filter, when the weight of the d double salt is obtained, the weight of potash is ascertained calculation.

It may, however, be much more readily arrived at by volumetr means as follows.

The potash having been converted into double chloride in t usual way is dried, collected, and mixed with about double its weight of pure sodic oxalate, and gently smelted in a platinum crucible; this operation results in the production of metallic platinum, chlorides of sodium and potassium, with some carbonate of soda. The quantity of potash present is, however, solely measured by the chlorine; in order to arrive at this, the fused mass is lixiviated with water, filtered, nearly neutralized with acetic acid, and the chlorine estimated with $\frac{N}{10}$ silver and chromate, the number of c.c. of silver required is multiplied by the factor 0·00157, which gives at once the weight of potash. This factor is used because 1 molecule of double chloride contains 3 atoms chlorine, hence the quantity of $\frac{N}{10}$ silver used is three times as much as in the case of sodic or potassic chloride.

2. Separation of the Potash as Bitartrate.

The mixed salts being rendered as nearly neutral as possible, a saturated solution of sodic bitartrate is added in excess, and the whole evaporated to dryness in the water bath. The dry mass is then deprived of the excess of sodic bitartrate by washing it on a filter with a saturated solution of potassic bitartrate; when all the soda salt has been removed, the potash salt is dissolved in hot water, and titrated with normal alkali, of which 1 c.c. represents 0·03911 gm. K.

SULPHURIC ACID AND SULPHATES.

Monohydrated Sulphuric Acid.

$H^2SO^4 = 98.$

Sulphuric Anhydride.

$SO^3 = 80.$

1. Mohr's Method.

§ 40. The indirect process devised by C. Mohr, and fully described in the "Annalen der Chemie und Pharmacie," Bd. 90, S. 165, depends upon the same method of determination as has already been described for the alkaline earths, that is to say, a known volume of baryta solution is added to the compound, more than sufficient to precipitate the sulphuric acid, the excess of baryta is converted into carbonate, and titrated with normal acid and alkali, as described in § 24.

It is best to use a normal solution of baric chloride as the precipitant, which is made by dissolving 122·05 gm. of pure chloride in the litre; this solution likewise suffices for the determination o sulphuric acid by the direct method.

The following is the method of procedure.

If the substance contains a considerable quantity of free acid, it must be brought near to neutrality by pure sodic carbonate; if alkaline, it must be slightly acidified with hydrochloric acid, a round number of c.c. of baryta solution is then added, and the whole digested in a warm place for some minutes; the excess of baryta is precipitated by a mixture of carbonate and caustic ammonia in slight excess; if a little piece of litmus paper be thrown into the mixture, a great excess can readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, thoroughly washed with boiling water, and titrated as in § 24.

The difference between the number of c.c. of baryta solution added, and that of normal acid required for the carbonate, will be the measure of the sulphuric acid present; each c.c. of baryta solution is equal to 0·040 gm. SO^3.

Example: 2 gm. pure and dry baric nitrate, and 1 gm. pure potassic sulphate were dissolved, mixed, and precipitated hot with carbonate and caustic ammonia; the precipitate, after being thoroughly washed, gave 1·002 gm. potassic sulphate, instead of 1 gm.

For technical purposes this process may be considerably shortened by the following modification, which dispenses with the washing of the precipitate.

The solution containing the sulphates or sulphuric acid is first rendered neutral—normal baric chloride is then added in excess, then normal sodic carbonate in excess of the baric chloride, and the volume of both solutions noted; the liquid is then made up to 200 or 300 c.c. in a flask, and an aliquot portion filtered off and titrated with normal acid, the difference between the baric chloride and sodic carbonate gives the sulphuric acid.

The solution must of course contain no substance precipitable by sodic carbonate except the baryta (or if so, it must be previously removed), nor must it contain any substance precipitable by baryta, such as phosphoric or oxalic acid, &c.

Another alkalimetric process suitable for technical purposes is that of Bohlig, see § 26.

2. Titration by Baric Chloride, and Potassic Chromate, (Wildenstein.)

To the hot solution containing the sulphuric acid to be estimated, (which must be neutral, or if acid, neutralized with caustic ammonia, free from carbonate,) a standard solution of baric chloride is added in slight excess, then a solution of potassic chromate, of known strength, is cautiously added to precipitate the excess of barium; so long as any barium remains in excess, the supernatant liquid is colourless, when it is all precipitated the liquid is yellow, from the free chromate; a few drops only of the chromate solution are necessary to produce a distinct colour.

Wildenstein uses a baric solution, of which 1 c.c. = 0·015 gm. of SO^3, and potassic chromate 1 c.c. = 0·010 gm. of SO^3. I prefer to use seminormal solutions, so that 1 c.c. of each is equal to 0·020 gm. of SO^3. If the chromate solution is made to possess the same chemical power as that of the baric chloride, the operator has simply to deduct the one from the other in analysis, in order to obtain the quantity of baric solution really required to precipitate all the sulphuric anhydride.

The Analytical process.—The substance or solution containing sulphuric acid is brought into a small wide-mouthed flask, diluted to about 50 c.c., acidified if necessary with hydrochloric acid, heated to boiling, and precipitated with a slight excess of standard baric chloride delivered from the burette; as the precipitate rapidly settles from a boiling solution, it is easy to avoid any great excess of barium, which would prevent the liquid from clearing so speedily; the mixture is then cautiously neutralized with ammonia free from carbonic acid, (to be certain of this, it is well to add to it two or three drops of calcic chloride or acetate solution).

The flask is then put over the lamp again, heated to boiling, and the chromate solution added in ½ c.c. or so, each time removing the flask from the lamp and allowing to settle, until the supernatant liquid is of a light yellow colour; the quantity of chromate is then deducted from the barium solution, and the remainder calculated for SO^3.

Or the mixture with barium in excess may be diluted to 100 or 150 c.c., the precipitate allowed to settle thoroughly, and 25 or 50 c.c. of the clear liquid taken out, heated to boiling, after neutralizing, and precipitated with chromate until all the barium is carried down as baric chromate, leaving the supernatant liquid of a light yellow colour; if there is any uncertainty in the first titration, the analysis may be checked by a second. The process has yielded me very satisfactory results in comparison with the barium method by weight;

it is peculiarly adapted for estimating sulphur in gas when burnt in the Letheby sulphur apparatus, details of which will be found in the section on Sulphur.

The presence of alkaline and earthy salts is of no consequence—zinc and cadmium do not interfere—nickel, cobalt, and copper give coloured ammoniacal solutions which prevent the yellow chromate being seen, but this difficulty can be overcome by the use of an external indicator for the excess of chromate. This indicator is an ammoniacal lead solution, made by mixing together, at the time required, one volume of pure ammonia and four volumes of lead acetate solution 1 : 20; the liquid has an opalescent appearance. To use the indicator, a large drop is spread upon a white porcelain plate, and one or two drops of the liquid under titration added; if the reddish yellow colour of lead chromate is produced, there is an excess of chromate, which can be cautiously reduced by adding more barium until the exact balance occurs.

3. Direct Precipitation with Normal Baric Chloride.

Very good results may be obtained by this method when carefully performed. The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the baric solution allowed to flow cautiously in from the burette until no further precipitation occurs. The end of the process can only be determined by filtering a portion of the liquid, and testing with a drop of the baric solution. Dr. Beale's filtering tube, shown in fig. 25, is a good aid in this case; a piece of Swedish filter paper is tied over the lower end, then some fine muslin to protect the paper, the tube is dipped about half an inch into the liquid, which rises through the filter perfectly clear; a little is to be poured into a test tube and a drop of baric solution added from the burette; if a cloudiness occurs, the contents of the tubes must be emptied back again, washed out into the liquid, and more baric solution added until all the sulphuric acid is precipitated; it is advisable to use a decinormal solution towards the end of the process.

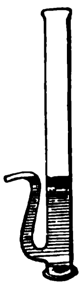

Fig. 25.

Instead of the test tube for ascertaining whether barium or sulphuric acid is in excess, a plate of black glass, or a sheet of colourless glass upon black paper may be used, upon which a drop of the clear solution is placed and tested by either a drop of baric chloride or sodic sulphate,—these testing solutions are preferably kept in two small bottles with elongated stoppers.

Wildenstein has arranged another method for the direct precipitation by barium, especially useful where a constant series of estimations have to be made. The apparatus is shown in fig. 26. A is a bottle of 900 or 1000 c.c. capacity, with the bottom removed, and made of well annealed glass so as to stand heating. B a thistle funnel bent round, as in the figure, and this syphon filter is put into action by opening the pinchcock below the cork. The mouth of the funnel is first tied over with a piece of fine cotton cloth, then two thicknesses of Swedish filter paper, and again with a piece of cotton cloth, the whole being securely tied with waxed thread.

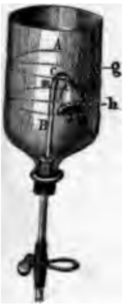

Fig. 26.

In precipitating SO^3 by baric chloride, there occurs a point similar to the so-called neutral point in silver assay, when in one and the same solution both barium and sulphuric acid after a minute or two produce a cloudiness. Owing to this circumstance, the barium solution must not be reckoned exactly by its amount of $Ba\,Cl^2$, but by its working effect, that is to say, the ending of the process must be that when the addition of a drop or two of barium solution gives no cloudiness after the lapse of two minutes.

The Analytical process.—The solution containing the SO^3 being prepared, and preferably in hydrochloric acid solution, the vessel A is filled with warm distilled water, and the pinchcock opened so as to fill the filter to the bend C; the cock is then opened and shut a few times so as to bring the water further down into the tube, but not to fill it entirely; the water is then emptied out of A, and about 400 c.c. of boiling distilled water poured in together with the SO^3 solution, then, if necessary, a small quantity of hydrochloric acid added, and the baric chloride added in moderate quantity from a burette. After mixing well, and waiting a few minutes, a portion is drawn off into a small beaker, and poured back without loss into A; a small quantity is then drawn off into a test tube, and two drops of baric chloride added; so long as a precipitate occurs, the liquid is returned to A, and more baric chloride added until a test is taken which shews no distinct cloudiness; the few drops added to produce this effect are deducted in the final calculation. If a distinct excess has been used, the analysis must be corrected with a solution of SO^3 corresponding in strength to the barium solution.

H 2

NITRIC ACID AND NITRATES.

Nitric Acid.

$HNO^3 = 63.$

Nitric Anhydride.

$N^2O^5 = 108.$

Factors.

Normal acid	×	0·063	$= HNO^3$
Ditto	×	0·054	$= N^2O^5$
Ditto	×	0·101	$= KNO^3$
Metallic iron	×	0·375	$= HNO^3$
Ditto	×	0·6018	$= KNO^3$

§ 41. The accurate estimation of nitric acid in combination presents great difficulties, and can only be secured by indirect means; the methods here given are sufficient for most purposes; very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

1. Gay Lussac's method modified by Abel (applicable only to Alkaline Nitrates.)

This process depends upon the conversion of potassic or sodic nitrates into carbonates by ignition with carbon, and the titration of the carbonate so obtained, by normal acid, as described in alkalimetry. The number of c.c. of normal acid required multiplied by 0·101, will give the weight of pure potassic nitrate in grammes; by 0·085, the weight of sodic nitrate in grammes.

The best method of procedure is as follows:—The sample is finely powdered and dried in an air bath, and 1 gramme, or an equivalent quantity in grains, weighed, introduced into a platinum crucible, and mixed with a fourth of its weight of pure graphite, (prepared by Brodie's process,) and four times its weight of pure ignited sodic chloride. The crucible is then covered and heated moderately for twenty minutes over a Bunsen's burner, or for eight or ten minutes in a muffle (the heat must not be so great as to volatilise the chloride of sodium to any extent). If sulphates are present they will be reduced to sulphides; and as these would consume the normal acid, and so lead to false results, it is necessary to sprinkle the fused mass with a little powdered potassic chlorate, and heat again moderately till all effervescence has ceased. The crucible is then set aside to cool, warm water added, the contents brought upon a filter, and washed with hot water till the washings are no longer alkaline. The filtrate is then titrated with litmus and normal acid in the ordinary way, or better by the residual method described in alkalimetry.

2. Acidimetric Method.

The principle of this mode of determining nitric acid is described in § 25, but is only applicable where the base is precipitable by pure or carbonated alkalies, and where no other acid is present, having a precipitable base; with nitrates of metallic oxides and alkaline earths, very accurate results are obtained.

3. Estimation of Nitrates by Distillation with Sulphuric Acid.

This method is of very general application, but particularly so with the impure alkaline nitrates of commerce; the process needs careful manipulation, but yields accurate results.

There are two methods of procedure.

a. To bring the weighed nitrate into a small tubulated retort with a cooled mixture of water and strong sulphuric acid, in the proportion of 10 c.c. of water and 5 c.c. of sulphuric acid for 1 gm. of nitrate; the neck of the retort is drawn out to a point and bent downward, entering a potash or other convenient bulb apparatus containing normal caustic alkali; the retort is then buried to its neck in the sand-bath, and heated to 170° C., (338° Fahr.) so long as any liquid distils over; the heat must never exceed 175° C. (347° Fahr.) otherwise traces of sulphuric acid will come over with the nitric acid. The quantity of acid distilled over is found by titrating the fluid in the receiver with normal acid as usual.

b. Distillation in a Partial Vacuum, (Finkener.) By this arrangement there is no danger of contaminating the distillate with sulphuric acid, inasmuch as the operation is conducted in a water bath, and when once set going needs no superintendence.

The retort is the same as before described, but the neck is not drawn out or bent; the stopper of the tubulure must be well ground. The receiver is a 200 c.c. flask with narrow neck, containing the requisite quantity of normal alkali diluted to about 30 c.c. The receiver is bound, air tight, to the neck of the retort, (which should reach nearly to the middle of the flask,) by means of a vulcanized tube: the proportions of acid and water before mentioned are introduced into the retort with a tube funnel. The stopper of the retort is then removed, and the contents, both of the receiver and retort, heated by spirit or gas lamps to boiling, so as to drive out the air; the weighed nitrate contained in a small tube is then dropped into the retort, the stopper inserted, the lamps removed, and the retort brought into the water bath, while the receiver is kept cool with wet tow or placed in cold water. The distillate is titrated as before; 1 or 2 gm. saltpetre require about four hours for the completion of the process. According to H. Rose, (Zeitschrift für an. Chem. Part 3, page 311,) Finkener obtained very accurate results by this method.

When chlorides are present in the nitrate a small quantity of moist oxide of silver is added to the mixture before distillation.

4. Estimation by conversion into Ammonia (Schulze and Vernon Harcourt.)

The principle of this method, is based on the fact that when a nitrate is heated with a strong alkaline solution and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Schulze found that when the zinc was platinised, or when sodium or aluminium amalgam was used, the reaction was perfect.—(Chem. Centr. blatt, 1861, pp. 657 and 833.) Vernon Harcourt and Siewert appear to have arrived independently at the same result, by using a mixture of iron and zinc.—(Journ. Chem. Soc., 1862, p. 381, An. Chem. u. Phar., 125, 293.)

As the latter process seems, on many accounts, preferable to that of Schulze, a short description of the apparatus devised by Harcourt is given. (Fig. 27).

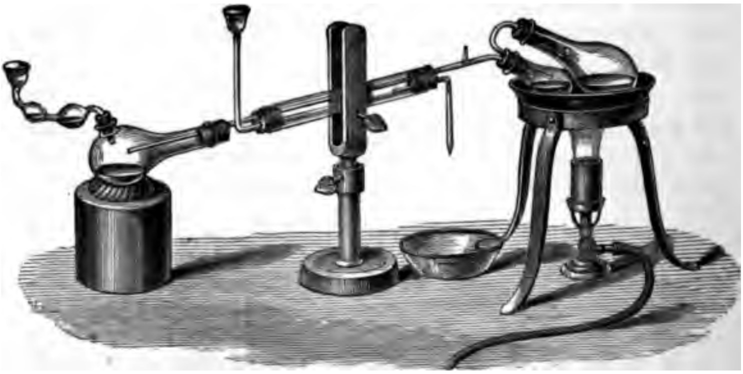

Fig. 27.

The distilling flask holds about 200 c.c., and is closely connected by a bent tube, with another smaller flask in such a manner that both may be placed obliquely upon a sand bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spirting of the boiling liquids from entering the exit tubes, but as a further precaution, these latter are in both flasks turned into the form of a hook; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser, (which may be made of wide glass tube,) into an ordinary tubulated receiver, containing normal sulphuric acid coloured with litmus; the end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid; instead of this latter, however, a chloride of calcium tube, filled with broken glass and moistened with acid, will answer the purpose: the distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a good fitting vulcanised tube; by this means water may be passed through the tube when the distillation is over, so as to remove any traces of ammonia which may be retained on its sides; all the corks of the apparatus should be soaked in hot paraffin, so as to fill up the pores.

All being ready, about 50 gm. of finely granulated zinc* (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) is put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible; the weighed nitrate is then introduced, either in solution or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sand-bath heated by a gas-burner, a little water being previously put into the second flask. Convenient proportions of material are ½ gm. nitre and about 20 c.c. each of water, and solution of potash of spec. grav. 1·3.

Heat is now applied to that part of the sand-bath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point; when distillation has actually commenced, the water in the second flask is made to boil gently; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may escape the first, are sure to be retained in the second flask. The distillation with the quantities above named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed, and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass; the contents of the receiver are then titrated with normal caustic potash or soda as usual.

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* After the distillation is over, the zinc and iron may be well washed, then dried, and preserved for the next operation.

Chlorides and sulphates do not interfere with the accuracy of the results.

A mean of several experiments with pure nitre gave 53·3% of nitric acid instead of 53·41%. The process does not give such accurate results with some metallic nitrates.

Siewert has suggested a modification of this process—the distilling apparatus is a 300—350 c.c. flask with tube leading to two small flasks connected together as wash bottles, and containing standard acid. For 1 gm. of nitre, 4 gm. of iron, and 10 gm. of zinc filings, with 16 gm. of caustic potash and 100 c.c. of alcohol of sp. gr. ·825, are necessary; after digesting for half an hour in the cold or in slight warmth, a stronger heat may be applied to drive out all the ammonia into the acid flasks; finally 10—15 c.c. of fresh alcohol is admitted to the distilling flask and distilled off to drive over the last traces of ammonia, and the acid solution then titrated residually as usual.

Chapman recommends the nitrate to be digested in cold solution containing a considerable quantity of caustic potash, with an unweighed excess of aluminium in thin sheet or filings; after the conversion is complete (say during a night,) the ammonia is distilled off into standard acid and estimated residually. Fuller details are given in Part 6, Estimation of nitric acid in waters.

Professor T. E. Thorpe prefers to use sheet zinc coated with copper for the reduction of nitrates and nitrites such as occur in water residues, &c., (Jour. Chem. Soc., 1873, p. 545). Thin sheet zinc is cleaned with dilute acid, then cut into small pieces and covered with a moderately strong solution of cupric sulphate in a beaker or flask, and the reduction of copper allowed to proceed until a thick brown deposition of copper occurs; the metals are washed three or four times with cold water, taking care to detach the copper as little as possible from the zinc, and are then placed in a suitable distilling flask holding about 100 c.c., the solution of nitrate is added, together with a small fragment of lime, and the ammonia formed by the reducing action of the metals distilled into an upright cylinder containing water, faintly acidulated with hydrochloric acid; a measured portion of the distillate is then titrated with Nessler test in the usual way. Further details are given in the section on Water Analysis. Part 6.

5. By Oxidation of Ferrous Salts. (Pelouze.)

The principle upon which this well-known process is based is as follows:

a. When a nitrate is brought in contact with a solution of ferrous oxide, mixed with free hydrochloric acid, and heated, part of the oxygen contained in the nitric acid passes over to the iron, forming a persalt, while the base combines with hydrochloric acid, and nitric oxide (NO^2) is set free; 3 eq. iron = 168 are oxidised by 1 eq. nitric acid = 63. If, therefore, a weighed quantity of the nitrate be mixed with an acid solution of ferrous chloride or sulphate, of known strength, in excess, and the solution boiled, to expel the liberated nitric oxide, then the amount of unoxidised iron remaining in the mixture, found by a suitable method of titration, the quantity of iron converted from ferrous into ferric oxide, will be the measure of the original nitric acid in the proportion of 168 to 63, or by dividing 63 by 168, the factor 0·375 is obtained, so that if the amount of iron changed as described be multiplied by this factor, the product will be the amount of nitric acid present.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of ferrous oxide absorbs oxygen from the atmosphere. On this account accurate results are only obtained by conducting hydrogen or carbonic acid gas through the apparatus while the boiling is carried on. This modification has been adopted by Fresenius with very satisfactory results. The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward, a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through the apparatus while it is being dissolved; the solution so obtained, or one of double sulphate of iron and ammonia of known strength being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for ten minutes or so, then boiled until the dark red colour of the liquid disappears, and gives place to the brownish yellow of ferric compounds; the retort is then suffered to cool, the current of carbonic acid or hydrogen still being kept up, then the liquid diluted freely and titrated with $\frac{N}{10}$ permanganate, as in § 28. Owing to the irregularities attending the use of permanganate with hydrochloric acid, it is preferable to dilute the solution less, and titrate with bichromate, as in § 31. Two grammes of pure iron, or its equivalent in double iron salt, 0·5 gm. of saltpetre and about 60 c.c. of strong hydrochloric acid, are convenient proportions for the analysis.

b. **Direct titration of the resulting ferric salt by stannous chloride.** Fresenius has adopted the use of stannous chloride for titrating the ferric salt with very good results.

The following plan of procedure is recommended by the same authority.

A solution of ferrous sulphate is prepared by dissolving 100 gm. of the crystals in 500 c.c. of hydrochloric acid of spec. grav. 1·10; when used for the analysis, the small proportion of peroxide of iron invariably present in it is found by titrating with stannous chloride, as in § 42.4. The nitrate being weighed or measured, as the case may be, is brought together with 50 c.c. (more or less, according to the quantity of nitrate) of the iron solution into a long necked flask, through the cork of which two glass tubes are passed, one connected with a carbonic acid apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The carbonic acid tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for ferric chloride, as in § 42.4. The liquid must, however, be suffered to cool before titrating with iodine for the excess of stannous chloride. While cooling, the stream of carbonic acid should still be continued. The quantity of iron changed into peroxide, multiplied by the factor 0·375, will give the amount of nitric acid.

Example: *a.* A solution of stannous chloride was used for titrating 10 c.c. of solution of pure ferric chloride, containing 0·215075 gm. of iron. 25·65 c.c. of tin solution were required, therefore that quantity was equal to 0·0807 gm. of HNO^3, or 0·069131 gm. of N^2O^5.

b. 50 c.c. of acid ferrous sulphate were titrated with tin solution for ferric oxide, and 0·24 c.c. were required.

c. 1 c.c. tin solution = 3·3 c.c. iodine solution.

d. 0·2177 gm. of pure nitre was boiled, as described, with 50 c.c. of the acid ferrous sulphate, and required 45·03 c.c. tin solution, and 4·7 c.c. iodine—

4·7 c.c. iodine solution = 1·42 c.c. $Sn.Cl^2$.
The peroxide in the protosulphate solution = 0·24 „
1·66

45·03—1·66=43·37, therefore 25·65 : 0·069131=43·37 : x, = 0·1169 N^2O^5 instead of 0·1163, or 53·69% instead of 53·41. A mean of this, with three other estimations, using variable proportions of tin and iron solutions, gave exactly 53·41%. The process is therefore entirely satisfactory.

c. **Direct Titration of the resulting Ferric Chloride by Iodine and Hyposulphite.** Mohr proceeds as follows.—The dry nitrate with twelve times its weight of double iron salt is placed in a 100—150 c.c. flask, with about 50 c.c. of hydrochloric acid and a little water. The flask is closed with a cork through which is passed a glass tube cut slant-wise below the cork; about 1¼ inch of stout vulcanised tube is then fixed over the upper end of the glass tube and closed with a piece of solid glass rod—a slit is cut vertically in the elastic tube so that when the contents of the flask boil the steam may escape from the valve so formed—the atmospheric pressure closes this valve when boiling ceases—the contents are boiled till all the nitric oxide is driven off and the solution is the colour of ferric chloride, then cooled, and a sufficiency of potassic iodide added to decompose the ferric chloride; when this is complete, starch is added, and the mixture titrated with hyposulphite; as the oxygen in nitric acid represents three times its equivalent of hyposulphite.

$$\frac{0{\cdot}0063}{3} = 0{\cdot}0021\ HNO^3 \text{ or } \frac{0{\cdot}0101}{3} = 0{\cdot}00337\ KNO^3$$

the quantity of hyposulphite used multiplied by these factors will give the quantity of nitric acid or potassic nitrate respectively. **Mohr** obtained by this method very reliable results.—(See also § 42.6.)

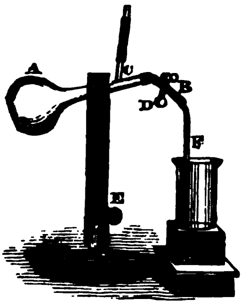

Fig. 28.

d. **Holland's Modification of the Pelouze process.**—The arrangement of apparatus shewn in fig. 28 obviates the use of an atmosphere of H or CO^2; A, is a long-necked assay flask drawn off at B, so as to form a shoulder, over which is passed a piece of stout pure india-rubber tube, D, about 6 centimetres long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the elastic connector D is placed a screw compression clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with the blow-pipe a piece of glass tube about 2 centimetres long, surmounted by one of stout elastic tube rather more than twice that length. The elastic tubes must be securely attached to the glass by binding with wire. After binding, it is as well to turn the end of the conductor back and smear the surface with fused caoutchouc, and then replace it to render the joint air-tight.

The Analytical Process:—A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water which washes all into the flask, the funnel is removed, and the flask supported by means of the wooden clamp, in the inclined position it occupies in the figure. The contents are now made to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c.

When this point is reached a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to escape through F.

Into the small beaker is put about 50 c.c., of a previously boiled solution of ferrous sulphate in hydrochloric acid. (The amount of iron already existing as persalt must be known.)

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it, when the whole has nearly receded the elastic tube is tightly compressed with the fingers, whilst the sides of the beaker are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than is necessary or admit air. Whilst F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion of the flask.

After heating in a water bath at 100° for half an hour the flask is removed from the water-bath and cautiously heated with a small flame, the fingers at the time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled, and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation the beaker is first removed, and then the lamp.

It now only remains to transfer the ferric solution to a suitable, vessel, and determine the perchloride with stannous chloride as in *b*.

A mean of six experiments for the percentage determination of N^2O^5 in pure nitre gave 53·53 per cent. instead of 53·41. The process is easy of execution, and gives satisfactory results. The point chiefly requiring attention is that the apparatus should be air-tight, which is secured by the use of good elastic tubes and clamp.

6. Schlösing's Method.

The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of ferrous chloride drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime; the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with normal alkali as usual.

This method was devised by Schlösing for the estimation of nitric acid in tobacco, and is especially suitable for that and similar purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0·15 gm., the process is very accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found either in the author's original paper, "Annal. de Chim.," 3 sér., tom. 40, 479, or "Journ. für pract. Chem.," 62, 142, also abridged in "Fresenius' Quantitative Analysis," sixth German, or second English edition. The process is less troublesome in practice than is generally supposed.

7. Estimation by conversion into Ammonia with Stannous Chloride, (Pugh.)

This process is based on the fact that when a nitrate is digested under pressure, and at a temperature of about 160° C. with an excess of stannous chloride and hydrochloric acid, the following reaction occurs :—

$$HNO^3 + 4SnCl^2 + 8HCl = NH^3 + 4SnCl^4 + 3H^2O.$$

1 eq. of nitric acid, therefore, under the above conditions, converts 4 eq. of tin from the state of proto to perchloride, consequently, if an unknown quantity of nitric acid be digested with a sufficient excess of stannous chloride of known strength, and the quantity changed into perchloride be afterward found by a suitable method of titration, the proportion of nitric acid will be found, supposing in all cases that no other substance is present, capable of effecting the same change in the tin solution.

Pugh arrived at the knowledge of the reaction described, by careful experiments, which are detailed in the Quarterly Journal of the Chemical Society, (vol. xii, part 1, page 35,) and used the process devised by Streng for titrating the strength of the tin solution, namely, potassic bichromate, potassic iodide, and starch. Experience has shown, however, that the estimation of tin by this method is far from satisfactory, owing to the variable amount of oxidation which the tin solution undergoes when different quantities of water or acid are present during the titration.

In my experiments on the process, I have therefore adopted the method of Lenssen (§ 52.) for estimating the strength of the tin solution, with the most satisfactory results, using in all cases an accurately weighed quantity of pure potassic nitrate for the analysis.

Example: *a.* A solution of pure nitre was prepared so that 1 c.c.=0·1 gm. KNO^3.

b. A solution of pure tin in hydrochloric acid, as in § 31·3.

c. A piece of stout combustion tube, about half an inch in diameter and fifteen inches long, was closed at one end, then heated before the blowpipe at about nine inches from the closed end, and drawn out for the space of an inch to a narrow neck; the tube was then cut off just above this neck, so as to leave a kind of funnel mouth.

d. 1 c.c. of the tin solution was measured with a very accurate pipette into a 500 or 600 c.c. flask; about 3 or 4 c.c. of saturated solution of Rochelle salt added; then a solution of pure sodic carbonate, till all effervescence was over, and the liquid clear and slightly alkaline; the sides of the flask were then washed down with cold distilled water, and about 20 c.c. of saturated solution of sodic bicarbonate delivered in; then starch liquor, and $\frac{N}{10}$ iodine solution from a $\frac{1}{10}$ c.c. burette, till the blue colour appeared. 17·9 c.c. were required, and as 1 c.c. of $\frac{N}{10}$ iodine corresponds to 0·0059 gm. tin, 1 c.c. of the tin solution contained 0·10561 gm. tin.

e. 2 c.c. of the solution *a* were then measured into the tube *c.* 14 c.c. of tin solution added, the funnel neck washed down with a few drops of water, a fragment of pure marble dropped in to evolve carbonic anhydride, and thus dispel all air from the tube; when the evolution of gas had ceased, the neck was heated and well closed; about two inches of space was thus left filled with carbonic anhydride. When the closed end was cold, the tube was shaken so as to mix the liquids well, put into a copper air bath, and heated to 160° C. for about fifteen minutes; then allowed to cool, and when perfectly cold the end of the tube broken off, the contents transferred to a large flask, and treated with the alkaline tartrate and carbonate, as in *d*; the tube was then washed through with cold distilled water into the flask, sodic bicarbonate in solution or in powder added, and the unchanged tin solution titrated with $\frac{N}{10}$ iodine, as described in *d*, the quantity required was 88·6 c.c. The calculation was therefore as follows.

1 c.c. tin solution=0·10561 gm. tin, consequently 14 c.c.= 1·47854 gm., from this must be deducted the weight of tin corresponding to 88·6 c.c. $\frac{N}{10}$ iodine = 0·52274 gm.. showing that 0·9558 gm. of tin had been oxidised by the nitric acid present; this in turn being multiplied by the factor 0·1144, (obtained by dividing the eq. weight of nitric acid by four times the eq. of tin,) gave 0·10934 gm. N^2O^5; theory requires that 0·2 gm. K,NO^3 should contain 0·10693 gm. In this case, therefore, the percentage of nitric acid in the salt was found to be 54·67, whereas it should be

53·41; but the mean of fifteen experiments made with variable quantities both of tin solution and nitrate, (always taking care that at least 10 eq. of tin were present for every one eq. of nitric acid,) gave 54·1% instead of 53·41.

The titration with iodine may be entirely dispensed with by distilling the ammonia from the tin solution after digestion, in the apparatus shown in fig. 19; in this case the liquid is simply neutralised with caustic soda or potash, brought into the distilling flask, an excess of caustic alkali added, the contents of the flask boiled, as in § 17, the ammonia received into normal acid, and titrated in the ordinary way.

Chapman and **Schenk** have found that in estimating nitrates in substances containing nitrogenous organic matter, such as sewage or other impure waters, **Pugh's** process is not reliable. Albumen, gelatine, or urea, evolve ammonia by digestion with stannous chloride without the latter being the least oxidised in the process.

In the case of water residues or other matters containing organic matter of a non-nitrogenous character, the nitric acid must not be estimated by the oxidation of the stannous salt, but by distillation of the ammonia.

When no organic matters affecting the tin solution are present, the process is very reliable. Gallic and pyrogallic acids or mannite have no reducing effect on the tin.

If sulphuric acid or a soluble sulphate is present in the substance digested with the solution of tin, sulphurous acid will be formed; baric sulphate is, however, not affected, consequently, it is necessary to precipitate the sulphuric acid by baric chloride, previous to digestion, when the method of estimation by iodine is used.

Crum's excellent method for the estimation of nitric acid as adopted by **Frankland** and **Armstrong** in the analysis of water residues, is fully described in the section on Water Analysis, Part 6.

8. Estimation by Indigo Solution.

This process originally devised by **Marx**, (Zeits. f. an. Chem. vol. vii, p. 412,) and afterwards modified and improved by **Goppelschröder** and others is a very ready and convenient one for estimating the nitrogen existing as nitrates, and nitrites in waters, &c.—but it is subject to great irregularity unless conducted with special precautions. The principle of the method is that of liberating free nitric and nitrous acids from their combinations by the aid of strong sulphuric acid, and measuring the quantity so liberated by the decoloration of a solution of indigo.

Having made some considerable number of experiments upon the process, and brought them in practice to a definite issue, I here give the necessary details for carrying out the process satisfactorily.

In the case of waters no interference is produced by the presence of chlorides, sulphates, or alkaline and earthy matters usually found.

This solution of indigo is best prepared from pure soluble indigo carmine, by dissolving it in distilled water in about such proportion that 10 c.c. is decolorized by 10 c.c. of a solution of potassic nitrate, containing 1·011 gm. per litre—these exact proportions are not necessary, but solutions agreeing closely with these quantities have been found to answer well. After dissolving the indigo, and finding its approximate strength by a standard solution of nitrate, it is advisable to heat it for an hour or two to a temperature of about 70° C, this prevents fungoid growth, and such a solution will keep well and of the same strength for an almost indefinite period, or, if a strongly acid solution is not objected to, the operator may add a moderate quantity of pure sulphuric acid, which has a similar preserving effect.

The fixing of the exact strength of the indigo, as compared with the standard nitrate solution, is a matter of great importance and is best done as follows :—

1·011 gm. of potassic nitrate is dissolved and made up to a litre for the standard nitrate solution, 10 c.c. of this liquid is measured into a boiling flask, and 25 c.c. of pure concentrated sulphuric acid (sp. gr. not less than 1·80) run into the flask quietly so that the fluids do not intimately mix, 10 c.c. of indigo are then run in and the whole shaken ; the temperature rises to probably 135° or 140°C. : if the blue colour is not discharged entirely, more nitrate solution may be cautiously dropped in immediately from a small pipette or burette so as to ascertain its probable strength, if on the other hand the colour is discharged, more indigo is at once measured in till either in the case of excess of indigo the blue, or in excess of nitrate, the brownish yellow, gives place to a light green colour. It is above all things necessary to keep the temperature up to not less than 120°C., and if necessary a small spirit lamp may be used to serve this purpose. The first titration will show the probable amount of indigo required for 10 c.c. of nitrate solution.

The final titration of the indigo is done by first mixing together 10 c.c. of nitrate solution with the measure of indigo found necessary in the first trial, and running into the mixture double its volume of sulphuric acid; this will probably show a deficiency of indigo, in which case a further quantity is at once cautiously added until the yellow colour gives place to a faint green.

With waters or other substances containing nitrates or nitrites the amount of nitrogen is approximately ascertained as in the case of titrating the indigo, and finally completed as just described; in all cases the volume of concentrated pure sulphuric acid must be not less than double that of the water or other nitrate solution and indigo taken together.

A standard solution of nitrate containing 1·0111 gm. of KNO^3 per litre will correspond to 0·140 gm. of N per litre, therefore, 10 c.c. of such solution will contain 0·0014 gm. or 1·4 milligramme of nitrogen.

9. Estimation of Ammonia and Nitrates by Conversion into Nitrogen Gas, with Bromised Sodic Hypochlorite.

Krocker and Dietrich have experimented upon this method originally devised by Knop, but instead of measuring the volume of nitrogen gas produced, which does not always give exact results, they use an excess of the oxidising agent, and after the action is complete, estimate the excess residually with $\frac{N}{10}$ arsenious solution and iodised starch paper, as in § 34. In the case of pure ammoniacal salts or nitrates the results are extremely satisfactory, and also with other compounds where there is nothing present to affect the bromised solution.

1. Preparation of the Chloro-bromous Solution.

One part of crystals of sodic carbonate is dissolved in 15 parts of cold distilled water, and chlorine gas passed through the solution till completely saturated; to the fluid is then added a sufficiency of 25 per cent. caustic soda solution to render the whole slippery when rubbed between the fingers. Bromine is then added to the mixture until a distinct lemon colour is produced. The addition of the bromine is, however, always preferably made just before the solution has to be used for a series of experiments.

2. Titration of the Solution.

10 c.c. are measured into a small beaker, diluted with distilled water, free from ammonia, and the $\frac{N}{10}$ arsenious solution allowed to

flow in with constant stirring, until a drop taken out with a glas rod and placed upon iodized starch paper produces no blue stain—towards the end of the process, the faint blue colour produce quickly disappears, therefore the effect must be observed imm diately the contact takes place.

Example: 10 c.c. of bromochlorous solution were titrated described with arsenious solution, and required 13·2 c.c. 55 c. also required 72·8 c.c.; therefore 1 c.c. bromised solution=1·3 c.c. arsenious solution.

The decinormal arsenious solution is so arranged that 1 c.c. = $\frac{1}{10000}$ eq. of Cl, Br, or I, and consequently of H; but as 1 eq NH^3 yields 3 eq. of H, 3 c.c. of arsenious solution represents $\frac{1}{1000}$ eq. of ammonia or nitrogen; and therefore 1 c.c. equals respectivel

$$\frac{0{\cdot}0014}{3} = 0{\cdot}0004666 \text{ gm. N},$$

$$\text{or } \frac{0{\cdot}0017}{3} = 0{\cdot}000566 \text{ gm. } NH^3$$

From these data it is of course easy to ascertain the relative value the bromised solution, as respects ammonia or nitrogen, by simp converting the number of c.c. used in any analysis into their valu as $\frac{N}{10}$ arsenious solution, and multiplying by the systematic coef cients given above; in fact, each analysis expresses itself in th form, since it is the volume of arsenious solution required whi represents the amount of ammonia or nitrogen present; thus Krocker's experiments, a solution containing 1 gm. of pure ammon chloride in the litre was used for estimation. The arsenio solution was not strictly decinormal, but was found by titrati with $\frac{N}{10}$ iodine solution to be slightly weaker, so that ea c.c. represented 0·000439 gm. of N, instead of 0·000466 gm. Twen c.c. of ammonia solution = 0·02 gm. of NH^4Cl, were placed in a beak diluted with pure distilled water, and 40 c.c. of bromised soluti added, and shaken for 10 minutes to liberate the nitrogen gas.

40 c.c. bromised solution =	52·8 c.c. $N^2As^2O^3$
Arsenious solution required for residual titration,	40·6 c.c.
	12·2 c.c.

12·2 × 0·000439 = 0·00535 gm. N. Calculation of form required = 0·00524 gm. N.

3. Treatment of Nitrates.

It has been seen in Harcourt's process, that nitric acid is converted into ammonia by means of zinc or iron in alkaline solution; this, however, occupies some considerable time. If, however, the action takes place in an acid instead of an alkaline solution, the effect is considerably hastened. To this end the authors use a flask fitted with a double bulb funnel, into which some dilute sulphuric acid is placed to absorb any traces of ammonia which might otherwise be carried away with the hydrogen.

The weighed or measured nitrate, or substance containing it, is placed in the flask with some zinc and diluted sulphuric acid, then closed with the safety funnel and allowed to stand for an hour; the contents are then transferred to a beaker, the washings of the funnel and flask added, and neutralised with sodic carbonate, then a measured excess of bromo-chlorous solution of known strength added and titrated residually with arsenious solution as before described. A series of experiments by the authors gave very exact numbers, with ammonic nitrate averaging 99·9% instead of 100.

IRON.

Fe = 56.

Factors.

1 c.c. $\frac{N}{10}$ permanganate, bichromate or hyposulphite = 0·0056 Fe
" " " = 0·0072 FeO
" " " = 0·0080 Fe^2O^3
" " " = 0·0392 Double iron salt.

1. Estimation in the Ferrous State.

§ 42. The estimation of iron in the ferrous state has already been incidentally described in §§ 28, 29, and 31. The present section is an amplification of the methods there given, as applied more distinctly to ores and products of iron manufacture, but before applying the permanganate or bichromate process to these substances, and since many operators prefer, with reason, to standardize such solutions upon metallic iron, especially for use in iron analysis, the following method is given as the best.

A piece of soft iron wire is well cleaned with scouring pape and about 1 gramme accurately weighed; this is placed into 250 c.c. boiling flask *a*, and 100 c.c. of dilute pure sulphuric aci (1 part concentrated acid to 5 of water) poured over it, about gramme of sodic bicarbonate is then added, and the apparatus fixe together as in fig. 29, the pinchcock remaining open ; the flask is closed by a tight fitting india rubber stopper, through which i passed the bent tube. The flask *c* contains 20 or 30 c.c. of pur distilled water, the flask *a* being supported over a lamp is gentl heated to boiling, and kept at this temperature until all the iron i dissolved, meanwhile about 300 c.c. of distilled water is boiled i a separate vessel to remove all air, and allowed to cool. As soo as the iron is dissolved, the lamp is removed, and the pinchcoc closed; when cooled somewhat, the pinchcock is opened, and th wash water suffered to flow back together with the boiled wate which is added to it until the flask is filled nearly to the mark the apparatus is then disconnected, and the flask *a* securely corke with a solid rubber cork, and suffered to cool to the temperatur of the room; finally the flask is filled exactly to the mark wit the boiled water, and the whole well shaken and mixed. Whe the small portion of undissolved carbon has subsided, 50 c.c. equa to $\frac{1}{5}$ the weight of iron taken, may be removed with the pipett for titration with the permanganate or bichromate.

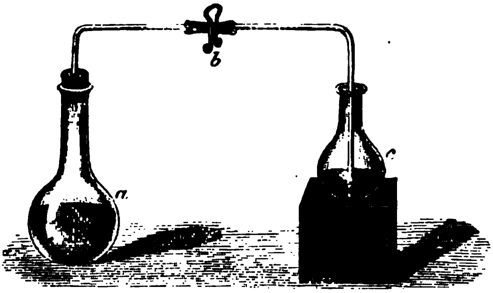

Fig. 29.

In the case of permanganate the 50 c.c. is freely diluted wit freshly boiled and cooled distilled water, and the standard solutio cautiously added from a tap burette, divided into $\frac{1}{5}$ or $\frac{1}{10}$ c.c. unti the rose colour is faintly perceived.

In the case of bichromate the solution should be less dilute and the titration conducted precisely as in § 31.

If the apparatus here described cannot be conveniently arrange for dissolving the metallic iron, the simple flask with elastic valv described in § 41.5 *c.*, or the apparatus shewn in fig. 30, may b used.

If the solution of permanganate or bichromate have been carefully prepared by weighing the purest re-agents, the probability is that they will be found exact in the titration when conducted as just described, allowing for the known average impurity in metallic iron, which may be taken at 0·4 per cent.; but in order to be absolutely secure in the working power of the solution, it is well to prove them thoroughly, and in case non-systematic solutions are used, it is of course absolutely necessary to do so. Therefore, supposing that 1·050 gm. of iron has been dissolved as above described, and the mean of three separate titrations has shown that 21·3 c.c. of permanganate has been required, the amount of pure iron converted by 100 c.c. of standard solution is found as follows:— $\frac{1·050}{5}$ = 0·210 gm. of iron wire, but as this is not pure iron, the following correction is necessary—0·210 × 0·996 = 0·20916 gm., which is the actual weight of pure iron—hence by the equation 21·3 c.c. : 0·20915 gm. = 100 c.c. : x gm. = 0·98197 gm., therefore 100 c.c. of such permanganate represents 0·98197 gm. pure metallic iron.

The same calculations are of course applicable to bichromate solution, but as the ending of the process is obtained by an external indicator, the titration should be repeated three or four times so as to insure the greatest accuracy.

The double iron salt is by far the most convenient material for adjusting standard solutions, and for use whenever pure ferrous compounds are wanted, but it must be most carefully made from pure materials, dried perfectly in the granular form, and kept from the light in small dry bottles, well corked. In this state it will keep for years unchanged, and only needs immediate solution in water for use. Even in the case of the salt not being strictly free from ferric oxide, due to faulty preparation, if it be once thoroughly dried, and kept as above described, its actual ferrous strength may be found by comparison with metallic iron, and a factor found for weighing it in system.

One cardinal point must never be forgotten, namely, that ferrous compounds are much more stable in sulphuric than in hydrochloric acid solution, and whenever possible, sulphuric acid should be used as the solvent; when hydrochloric acid must be used, strict attention should be given to the precautions mentioned on page 65.

2. Estimation of the Percentage of Pure Iron in Steel, Cast and Wrought Iron, Spiegeleisen, &c.—Mohr's Method.

Instead of the hitherto common method of separately estimating the impurities in samples of manufactured iron and steel, this process is adapted to the delicate estimation of the iron itself, and is similar in principle to the assay of silver by Gay Lussac's method, that is to say, the analysis is so arranged that the greatest accuracy shall be secured.

The standard solutions of potassic bichromate, of which there are two, are so prepared that 100 c.c. or dm. of the first will exactly convert respectively 1 gm. or 10 grains of iron into peroxide; the second, or decimal solution, is one-tenth the strength of the first.

The solution of bichromate No. 1 is prepared by dissolving 8·785 gm. of the pure salt in 1 litre, or 87·85 grn. in 10,000 grains of distilled water at 16° C. The decimal solution No. 2 is made by taking 100 c.c. of No. 1 and diluting it to 1 litre, or 100 decems to 10,000 grains, therefore—

100 c.c. or dm. of No. 1=0·01 gm. or 0·1 grn. Iron.
100 c.c. or dm. of No. 2=0·001 gm. or 0·01 grn. ditto.

The Analytical Process. The sample of iron to be examined is reduced to powder in a hardened steel mortar, or if in the form of wire, or in a soft state, cut into small pieces, and exactly 1·050 gm. or 10·50 grn. weighed off; this is brought into the apparatus, fig. 29, or some similar arrangement, and dissolved in pure hydrochloric or sulphuric acid. When the solution is accomplished, 100 c.c. or dm. of bichromate solution No. 1 (containing 0·8785 gm. or 8·758 grn. of bichromate, which is exactly sufficient to peroxidise respectively 1 gm. or 10 grn. of pure iron) is added; the decimal solution is then added from a small burette, until a drop of the mixture, brought in contact with red potassic prussiate, no longer produces a blue colour; the analysis is then calculated in the usual way.

Example: 1·05 gm. of Bessemer steel was dissolved in pure sulphuric acid, 100 c.c. of bichromate No. 1 added, and afterwards 39 c.c. of No. 2 required for complete oxidation; consequently there were 1·039 gm. of pure iron contained in the 1·050 gm. taken for analysis; this is equal to 989·4 parts per thousand, or 98·94 per cent.

Instead of the empirical solutions here described, the ordinary decinormal and centinormal solutions of bichromate, or permanganate may be employed with equal accuracy. As 100 c.c. of decinormal solution is equal to 0·56 gm. of pure iron, it is necessary that somewhat more than this quantity of the sample should be weighed, say 0·58 or 0·60 gm. 100 c.c. of decinormal solution are then added, and the analysis completed with the centinormal solution.

3. Reduction of Ferric Compounds to the Ferrous State.

This may be accomplished by metallic zinc, (§ 29) for use with permanganate, or by stannous chloride, (§ 31), for bichromate solution. Some operators use other reducing agents, such as sodic sulphite or hyposulphite, hydric sulphide or ammonic sulphide, &c., but the zinc or tin methods are simpler and better. In the case of zinc being used, the metal must either be free from iron, or if it contain any, the exact quantity must be known and allowed for, and further, the pieces of zinc used must be entirely dissolved before the solution is titrated.

In the case of stannous chloride the solution must be clear, and is best made stronger than that mentioned in § 31.3, say 10 to 15 gm. per litre; the point of exact reduction in the boiling hot liquid may be known very closely by the discharge of colour in the ferric solution, but may be made sure by the use of a freshly made solution of potassic sulphocyanide spread in drops on a white plate, care being taken to lose no time in bringing the drop of iron solution in contact with the test, in order to avoid re-oxidation from the air. The occurrence of a faint pink tinge may be accepted as an evidence of the proper point; when this occurs, two or three drops of the standard bichromate may be added to the solution, and another test made, if this shews a slight, but nevertheless distinct accession of colour with the sulphocyanide, the absence of stannous salt in excess is proved, and the titration should be commenced at once.

ESTIMATION IN THE FERRIC STATE.

4. Direct Titration of Iron by Stannous Chloride.

The reduction of iron from the ferric to the ferrous state by this reagent has been previously referred to, and it will be readily seen that the principle involved in the reaction can be made available for a direct estimation of iron, being, in fact, simply a reversion of the ordinary process by permanganate and bichromate.

Fresenius has recorded a series of experiments made on the weak points of this process, and gives it as his opinion, that it is most accurate and reliable with proper care, without which, of course, no analytical process whatever is worth anything. The summary of his process is as follows:—

a. A solution of ferric oxide of known strength is first prepared, by dissolving 10·04 gm. of soft iron wire (= 10 gm. of pure iron) in pure hydrochloric acid, adding potassic chlorate to complete oxidation, boiling till the excess of chlorine is removed, and diluting the solution to 1 litre.

b. A clear solution of stannous chloride, of such strength that about one volume of it and two of the iron solution are required for the complete reaction. See § 31, 3.

c. A solution of iodine in potassic iodide, containing about 0·010 gm. of iodine in 1 c.c. (if the operator has the ordinary decinormal iodine solution at hand, it is equally applicable). The operations are as follows:—

1. 1 or 2 c.c. of the tin solution are put into a beaker with a little starch liquor, and the iodine solution added from a burette till the blue colour occurs; the quantity is recorded.

2. 50 c.c. of the iron solution = 0·5 gm. of iron, are put into a small flask with a little hydrochloric acid, and heated to gentle boiling (preferably on a hot plate), the tin solution is then allowed to flow in from a burette until the yellow colour of the solution is nearly destroyed, it is then added drop by drop, waiting after each addition until the colour is completely gone and the reduction ended. If this is carefully managed, there need be no more tin solution added than is actually required; however, to guard against any error in this respect, the solution is cooled, a little starch liquor added, and the iodine solution added by drops until a permanent blue colour is obtained. As the strength of the iodine solution compared with the tin has been found in 1, the excess of tin solution corresponding to the iodine used is deducted from the original quantity, so that by this means the volume of tin solution corresponding to 0·5 gm. of iron is found.

The operator is, therefore, now in a position to estimate any unknown quantity of iron which may exist, in a given solution, in the ferric state by means of the solution of tin.

If the iron should exist partly or wholly in the state of ferrous oxide, it must be oxidised by the addition of potassic chlorate, and boiling to dissipate the excess of chlorine, as described in *a*.

Example: 50 c.c. of iron solution, containing 0·5 gm. of iron, required 25 c.c. of tin solution.

A solution, containing an unknown quantity of iron was then taken for analysis, which required 20 c.c., consequently a rule of three sum gave the proportion of iron as follows:—

$$25 : 0{\cdot}50 \text{ gm.} :: 20 : 0{\cdot}40 \text{ gm.}$$

It must be remembered that the solution of tin is not permanent, consequently it must be tested every day afresh. Two conditions are necessary in order to ensure accurate results.

1st. The iron solution must be tolerably concentrated, since the end of the reduction by loss of colour is more distinct; and further, the dilution of the liquid to any extent interferes with the quantity of tin solution necessary to effect the reduction. Fresenius found that by diluting the 10 c.c. of iron solution with 30 c.c. of distilled water, 0·1 c.c. more was required than in the concentrated state. This is, however, always the case with stannous chloride in acid solution, and constitutes the weak point in Streng's method of analysis by its means; it would seem that dilution either predisposed it to rapid oxidation, or that water had the power within itself to communicate a certain proportion of oxygen to it.

2nd. The addition of the tin solution to the iron must be so regulated that only a very small quantity of iodine is necessary to estimate the excess—if this is not done another source of error steps in, namely, the influence which dilution, on the one hand, or the presence of great or small quantities of hydrochloric acid on the other, are known to exercise over this reaction; practically, it was found that where the addition of tin, to the somewhat concentrated iron solution, was cautiously made so that the colour was just discharged, the mixture then rapidly cooled, starch added and then iodine till it became blue, the estimation was extremely accurate.

5. Titration of Ferric Salts by Sodic Hyposulphite.

SCHERER first suggested the direct titration of iron by hyposulphite, which latter was added to a solution of ferric chloride until no further violet colour was produced. This was found by many to be inexact, but Kremer (Journ. f. Pract. Chem., 84, 339) has made a series of careful experiments, the result of which is that the following modified method can be highly recommended.

The reaction which takes place between sodic hyposulphite and ferric chloride is such as to produce ferrous chloride, sodic tetrathionate. and sodic chloride. $2S^2O^3Na^2 + Fe^2Cl^6 + 2HCl = S^4O^6H^2 + 4NaCl + 2FeCl^2$. The hyposulphite, which may conveniently be of $\frac{N}{10}$ strength, is added in excess, and the excess determined by $\frac{N}{10}$ iodine and starch liquor.

The Analytical process: The iron solution, containing not more than 1 per cent. of metal, which must exist in the ferric state without any excess of oxidising material (best obtained by adding concentrated potassic permanganate until the red colour is produced, then boiling till both that and any free chlorine is expelled), is moderately acidified with hydrochloric acid, sodic acetate added till the mixture is red, then dilute hydrochloric acid until the red colour disappears; then diluted till the iron amounts to ¼ or ⅛ per cent., and $\frac{N}{10}$ hyposulphite added in excess, best known by throwing in a particle of potassic sulphocyanide after the violet colour produced by the hyposulphite has disappeared; if any red colour occurs, more hyposulphite must be added. Starch liquor and $\frac{N}{10}$ iodine are then used to ascertain the excess of hyposulphite; each c.c. of the latter is equal to 0·0056 gm. iron. A mean of several experiments gave 100·06 Fe, instead of 100.

Oudemanns' Method. A simpler process for the direct titration of iron by hyposulphite has been devised by Oudemanns (Zeitschrift für an. Chem. vol. vi, p. 129, and the same, vol. ix p. 342), which gives very good results.

The Analytical process: To the dilute ferric solution, which should not contain more than 0·1 to 0·2 gm. of Fe in 100 c.c., nor much free hydrochloric acid, 3 c.c. of 1 per cent. solution of cupric sulphate is added, 2 c.c. of concentrated hydrochloric acid, and to about every 100 c.c. of fluid, 1 c.c. of a 1 per cent. solution of potassic sulphocyanide.

The mixture may with advantage be very slightly warmed, and the hyposulphite delivered in from the burette at first pretty freely—the red colour produced by the sulphocyanide gradually fades away as this occurs, the hyposulphite must be added in smaller quantities constantly agitating the liquid until it becomes as colourless as pure water. If any doubt exists as to the exact ending, a slight excess of hyposulphite may be added, and the quantity found by $\frac{N}{10}$ iodine and starch. Greater accuracy will always be insured by adding hyposulphite in excess, then starch liquor, and titrating backward with iodine till the blue colour appears.

The accuracy of the process is not interfered with by the presence of salts of the alkalies, strontia, lime, magnesia, alumina or manganous oxide; neither do salts of nickel, cobalt, or copper, unless their quantity is such as to give colour to the solution,

Oudemanns believes that the small proportion of copper solution added has a kind of catalytic effect in determining the reduction of the iron. This appears, however, doubtful, since Popp (Zeitschrift fur Chem. von Beilstein, No. 11, 1870), states that equally good effects are obtained by omitting the copper and heating the solution to 40° C. The original process with copper does not necessarily require any heating, and this favours Oudemanns' view.

The process is a rapid one, and with care gives very satisfactory results.

The free iodine is titrated with hyposulphite and starch, 1 c.c. $\frac{N}{10}$ hyposulphite = 0·0127 gm. of I., or 0·0056 gm. of Fe.

6. Estimation by Potassic Iodide and Sodic Hyposulphite.

When ferric chloride is digested with potassic iodide in excess, iodine is liberated which dissolves in the free potassic iodide—

$$FeCl^3 + KI = FeCl^2 + KCl + I.$$

The Analytical Process:—The hydrochloric acid solution, which must contain no free chlorine or nitric acid, and all the iron in the ferric state, is nearly neutralised with caustic potash or soda, transferred to a well-stoppered flask, and an excess of strong solution of potassic iodide added; it is then heated to 50° or 60° C. on the water-bath, closely stoppered, for about twenty minutes; the flask is then cooled, starch liquor added, and titrated with hyposulphite till the blue colour disappears. This process gives very satisfactory results in the absence of all substances liable to affect the potassic iodide, such as free chlorine or nitric acid, and is particularly serviceable for estimating small quantities of iron.

7. Estimation of Iron by Colour Titration.

This method, which approaches in delicacy the Nessler test for ammonia, is applicable for very minute quantities of iron, such as may occur in the ash of bread when testing for alum, water residues, and similar cases: with care very exact results are to be obtained.

It is first necessary to have a standard solution of iron in the ferric state, which can be made by dissolving 1·004 gm. of iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing and re-dissolving the ferric oxide in a little hydrochloric acid, then diluting to 1 litre. 1 c.c. of this solution contains 1 milligramme of pure iron in the form of ferric chloride; it may be further diluted, when required, so as to contain $\frac{1}{10}$ milligramme in a c.c., as in the case of ammonia solution for Nesslerising.[*] The solution used for striking the colour is potassic ferrocyanide dissolved in water 1 : 20.

Example: The material containing a minute unknown quantity of iron, say a water residue, is dissolved in hydrochloric acid, and diluted to 100 c.c., or any other convenient measure. 10 c.c. are placed into a white glass cylinder marked at 100 c.c., 1 c.c. of concentrated nitric acid added, (the presence of free acid is always necessary in this process,) then diluted to the mark with distilled water, and well stirred.

---

[*] A solution of the same strength can also be made by weighing 0·7 gm. of pure ferrous-ammonic sulphate, dissolving in water, acidifying with sulphuric acid, adding sufficient permanganate solution to convert the iron exactly into ferric salt, then diluting to 1 litre.

1 c.c. of ferrocyanide solution is then added, well mixed, and allowed to stand at rest a few minutes to develop the colour.

A similar cylinder is then filled with a mixture of, say, 1 c.c. of standard iron solution, 1 c.c. nitric acid and distilled water, and 1 c.c. ferrocyanide added; if this does not approach the colour of the first mixture, other quantities of iron are tried until an exact similarity of colour occurs; the exact strength of the iron solution being known, it is easy to arrive at the quantity of pure iron present in the substance examined, and to convert it into its state of combination by calculation.

IRON ORES.

§ 43. In the analysis of iron ores it is very often necessary to determine not only the total amount of iron, but also the state in which it exists; for instance, magnetic iron ore consists of a mixture of the two oxides in tolerably definite proportions, and it is sometimes advisable to know the quantities of each.

In order to prevent, therefore, the further oxidation of the ferrous oxide, and so leading to false results, the little flask apparatus (fig. 30) adapted by Mohr is highly recommendable, or fig. 29 is equally serviceable.

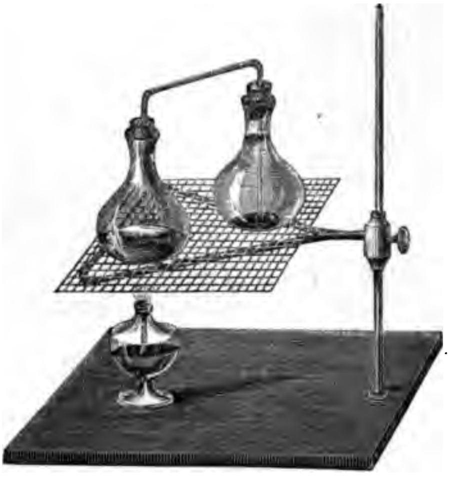

Fig. 30.

The left hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid is added; the other flask contains distilled water only, the tube from the first flask entering to the bottom of the second. When the ore is ready in the flask and the tubes fitted, hydrochloric acid is poured in, and a few grains of sodic bicarbonate added to produce a flow of carbonic acid; the air of the flask is thus dispelled, and as the acid dissolves the ore, the gases evolved drive out in turn the carbonic acid, which is partly absorbed by the water in the second flask. When the ore is all dissolved and the lamp removed, the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that, in the majority of cases, it is ready for immediate titration; if not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added.

When the total amount of iron present in any sample of ore has to be determined, it is necessary to reduce any peroxide present to the state of protoxide by zinc, or stannous chloride, as previously described.

1. Magnetic Iron Ore.

The ferrous oxide is determined first by means of the apparatus, fig. 29 or 30. The ore is put into the vessel in a state of fine powder, strong hydrochloric acid added, together with a few grains of sodic bicarbonate, and heat applied gently with the lamp until the ore is dissolved, then diluted if necessary, and titrated with potassic bichromate or permanganate.

Example: 0·5 gm. of ore was treated as above, and required 19·5 c.c. of $\frac{N}{10}$ bichromate, which multiplied by 0·0056, gave 0·1092 gm. of iron=0·1404 gm. of ferrous oxide=28·08 per cent.

The ferric oxide was now found by reducing 0·5 gm. of the same ore with zinc, and estimating the total iron present, the quantity of bichromate required was—

59 c.c. $\frac{N}{10}$=0·3304 gm. total Fe
Deduct 0·1092 „ as FeO

Leaving 0·2212 „ as Fe^2O^3

The result of the analysis is, therefore—

Ferrous oxide	28·08 per cent.
Ferric oxide	63·20 „
Difference (Gangue, &c.) . .	8·72 „
	100·00

2. Spathose Iron Ore.

The total amount of ferrous oxide in this carbonate is ascertained directly by solution in hydrochloric acid; as the carbonic acid evolved is generally sufficient to expel all air, the tube dipping under water may be dispensed with. Should the ore be very impure, zinc may have to be added in order to ensure the reduction of all the iron present.

As the ore contains in most cases the carbonates of manganese, lime, and magnesia, these may all be determined, together with the iron, as follows—

A weighed portion of ore is brought into solution in hydrochloric acid, and filtered, if necessary, to separate insoluble silicious matter.

The solution is then boiled, with a few drops of nitric acid to peroxidise the iron, diluted, and sodic carbonate added in sufficient quantity to precipitate the ferric oxide, then sodic acetate, and the whole boiled that the precipitate may become somewhat dense and separate from the liquid; filter, and if necessary, reduce the oxide of iron after careful washing, with zinc, or stannous chloride, and determine with permanganate or bichromate.

The filtrate containing the other bases is treated with sodic hypochlorite covered and set aside for twenty-four hours in order to precipitate the manganese as hydrated oxide, which is collected and titrated as in § 46.

The filtrate from the last is mixed with ammonic oxalate to precipitate the lime, which is estimated by permanganate, as in § 49.

The filtrate from the lime contains the magnesia, which may be precipitated with sodic phosphate and ammonia, and the precipitate weighed as usual or titrated with uranium solution.

Red and brown hematites can be examined in a similar manner to the foregoing.

3. Chrome Iron Ore.

This material is of great commercial importance, as being the source of potassic bichromate.

The ore varies considerably in quality, some samples being very rich, while others are very poor in chromium. In all cases the sample is to be first of all brought into *very fine* powder. About a gramme is rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar.

a. **O'Neill's Process:** The very finely powdered ore is fused with ten times its weight of potassic bisulphate for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is then transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved; no black residue must occur, otherwise the ore is not completely decomposed; sodic carbonate is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the ashes and precipitate mixed with about twelve times the weight of the original ore, of a mixture of two parts potassic chlorate and three parts sodic carbonate, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as in § 57.

The oxide of iron remaining on the filter is titrated, if required, by any of the methods described in §§ 42, 43.

b. **Britton's Process.** Reduce the mineral to the finest state of division possible in an agate mortar. Weigh off 0·5 gm., and add to it 4·0 gm. of flux, previously prepared, composed of one part potassic chlorate and three parts soda-lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright red-heat for an hour and a half or more. The mass will not fuse, but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and turn the powder into a tall 4 oz. beaker, and add about 18 c.c. of hot water, and boil for two or three minutes; when cold, add 15 c.c. of hydrochloric acid, and stir with a glass rod for a few minutes, till the solid matter, with the exception, probably of a little silica in a flaky gelatinous state, becomes dissolved. Both the iron and chromium will then be in the highest state of oxidation—Fe^2O^3 and Cr^2O^3. Pour the fluid into a white porcelain dish of about 20 oz. capacity, and dilute with washings of the beaker to about 3 oz. Immediately after, also, add cautiously 1 gm. of metallic iron of known purity, or an equivalent quantity of double iron salt, previously dissolved in dilute sulphuric acid, and further diluted with cold water to about 5 oz., to make up the volume in the dish to about 8 oz., then determine, volumetrically, with $\frac{N}{10}$ permanganate, the amount of ferrous oxide remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidised to sesquioxide by the chromic acid. Every one part so oxidised will represent 0·320 of metallic chromium, or 0·4663 of sesquioxide, Cr^2O^3, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder, as already directed, dissolve it by adding, first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of hydrochloric acid, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure metallic zinc sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease, and the zinc has become quite dissolved; then nearly fill the tube with *cold* water, acidulated with 1-10th of sulphuric acid, and pour the contents into the porcelain dish, add *cold* water to make up the volume to about 8 oz., and complete the operation with the standard permanganate solution.

4. Estimation of Iron in Silicates.

Wilbur and Whittlesey (Chem. News, vol. xxii. p. 2), give a series of determinations of iron existing in various silicates, either as mixtures of ferric and ferrous salts or of either separately, which appear very satisfactory.

The very finely powdered silicate is mixed with rather more than its own weight of powdered fluor spar or cryolite (free from iron), in a platinum crucible, covered with hydrochloric acid and heated on the water bath until the silicate is all dissolved. During the digestion either carbonic acid gas or coal gas free from H^2S is supplied over the surface of the liquid so as to prevent excess of air—when decomposition is complete (the time varying with the nature of the material), the mixture is diluted and titrated with permanganate in the usual way for ferrous oxide; the ferric oxide can then be reduced by zinc and its proportion found.

By Hydrofluoric acid (Early's process): Two grammes of the finely powdered silicate are placed in a deep platinum crucible, and 40 c.c. of hydrofluoric acid (containing about 20% HF) added. The mixture is heated to near the boiling point and occasionally stirred with a platinum wire until the decomposition of the silicate is complete, which occupies usually about ten minutes. 10 c.c. of pure H^2SO^4 diluted with an equal quantity of water are then added, and the heat continued for a few minutes. The crucible and its contents are then quickly cooled, diluted with fresh boiled water and the ferrous salt estimated with permanganate or bichromate as usual.

If the hydrofluoric acid has been prepared in leaden vessels it invariably contains SO^2, in such cases it is necessary to add to it, previous to use, some concentrated solution of permanganate so as to oxidise the SO^2.

The process is a rapid and satisfactory one, yielding much more accurate results than the method of fusion with alkaline carbonates or acid potassic sulphate.

5. Estimation of Iron by Cuprous Chloride (Winkler).

Cuprous chloride is capable of reducing ferric to ferrous compounds completely at ordinary temperatures. The loss of yellow colour may, to a certain extent, be taken as the ending of the process, but as the operation is, owing to many reasons, best conducted in dilute solution, it is better to use potassic sulphocyanide as an indicator. There is one very serious drawback to the process arising from the instability of the copper solution, it is so sensitive to the presence of oxygen as scarcely to bear pouring into a burette without losing its colourless condition, and becoming blue from the presence of cupric chloride. By a careful arrangement of apparatus this defect may be greatly remedied, and it is convenient in the technical examination of iron ores to be able to ascertain quickly and in the cold, the approximate amount of iron existing in the ferric state in any given solution.

Cobalt, nickel, copper, or arsenic are of no consequence in moderate quantity, especially as the solution used in the analysis is very dilute—in fact, nothing interferes except such metals as would be reduced in the same way as iron.

The solution of cuprous chloride is made by taking equal weights of cupric nitrate and sodic chloride, dissolving in water in a boiling flask, adding hydrochloric acid freely, then clean sheet copper in spiral strips, and heating the whole to boiling on a sand bath till nearly or quite colourless. The flask, tightly corked, is removed to a cool place, and when cold diluted with water which has been boiled and cooled containing about 10 per cent. of hydrochloric acid, till on titrating the solution roughly it is found that 1 c.c. is necessary to reduce about 0·006 gm. Fe.

The solution is then transferred quickly to a well-stoppered bottle, which already contains a clean spiral of stout copper wire reaching quite to the stopper. The solution will constantly undergo some little change, but if its strength be established before each set of experiments in any one day, it is sufficiently exact. The standard solution of ferric chloride may be the same as is described in § 42. 4*a*.—10 c.c. of which will contain 0·1 gm. Fe.

The Analytical process: Ten c.c. of the ferric solution are diluted with 400 or 450 c.c. of water, and to it are added 5 drops of saturated solution of potassic sulphocyanide, with a small pipette, and 10 c.c. of hydrochloric acid.

The solution is then brought under the burette containin the copper solution, and is dropped in cautiously until the re colour just disappears—any excess of copper solution after thi point occurs produces a cloudiness from the presence of cuprou sulphocyanide. There are, therefore, two indications of the en of the reaction.

If the copper solution is not of the right strength, namely, abou 14 or 15 c.c. to the 10 c.c. of iron solution, it must be adjusted b either diluting with fresh boiled and cooled water containing abou 10 per cent. of hydrochloric acid, or strengthened by the addition c cuprous chloride in concentrated solution.

6. Estimation of Iron in Ores by Comparison with the same weigh of Pure Iron.

This method is fully explained in § 3, and is, of course applicable to any substance which can be obtained tolerably pure such as soft iron wire, the titrating solution may be either potassi permanganate or bichromate of unknown strength.

COPPER.

Cu = 63·5.

Factors for converting the quantity of Iron represented by Permanganate, Bichromate, or Hyposulphite into Copper.

1 c.c. $\frac{N}{10}$ solution = 0·00635 gm. Copper
Iron × 1·1314 = Copper
" × 1·4171 = Cupric oxide
" × 4·453 = Crystallised cupric sulphate
Double Iron Salt × 0·16163 = Copper
" " × 0·2024 = Cupric oxide
" " × 0·6351 = Crystallised cupric sulphate.

§ 44. So many methods have been proposed for the volumetri estimation of copper that the analyst is bewildered by their numbe and hardly knows upon which to depend.

My own opinion is that in many cases it is safer and les troublesome to estimate the metal by weight; there are, howevei instances where volumetric methods can be applied with advantage and the following processes are chosen as the best.

1. Method of separating Copper from any of its Ores for Residues in a pure Metallic state, so that it may be weighed direct or estimated by Volumetric methods.

The substance must be brought into very fine powder, particularly if it contain sulphur, and about 5 gm. of it weighed, placed in a deep porcelain crucible or capsule about 4 in. in diameter, and covered with a concentrated mixture of nitric and sulphuric acids, and water added cautiously; a larger quantity of nitric acid is necessary when sulphur is present (as in pyrites,) than in other cases; a watch glass or another capsule is placed upon the top of that containing the mixture so as to prevent loss by spirting—preferably a large watch glass with a hole drilled in the middle. Heat is then applied to boiling and continued till the mass is nearly dry, the cover is then removed, and if not washed clean by the steam produced in the operation itself, is washed with a small quantity of water into the mass, which is again evaporated to dryness; the heat is then increased until all acid vapours are expelled, and the capsule set aside to cool. In the case of pyrites the heat must be continued long enough to burn off the sulphur, the capsule may then be slightly cooled and nitric acid again added, and the burning repeated; in certain cases this may be necessary a third time in order to oxidise all sulphur and extraneous matter.

By this treatment the copper is obtained as sulphate, the iron mostly as insoluble basic sulphate, lead as insoluble sulphate, antimony and tin also insoluble; zinc, cobalt, and nickel are of no consequence in the following treatment. The cold residue is covered with water and boiled till all soluble matter is extracted, then filtered through a small filter into a weighed platinum dish, the residue being washed clean with boiling water; the dish, with its contents, is placed on the water-bath or over a small spirit lamp, gently heated, acidified with hydrochloric acid, and a small lump of pure zinc added to reduce the copper to the metallic state; there must be sufficient acid to produce a distinct evolution of hydrogen, and the dish covered with a watch glass to prevent loss of liquid by spirting, the glass afterwards being rinsed into the liquid. The reduction is in all cases better done by a separate battery cell as almost all zinc leaves some residue. The end of the reduction is best known by taking a drop of the supernatant liquid out with a glass rod, and touching the surface of some acidulated sulphuretted hydrogen water or dilute potassic ferrocyanide contained in a small white capsule; if no brown colour is produced, the reduction is ended and any undissolved zinc can either be removed mechanically with a pair of forceps, taking care to free it from any adhering copper, or dissolved by the addition of fresh acid. The precipitated copper, if pure and clean, will possess a rose red colour; it must be quickly washed with boiling water to free it from acid—the first washings should be poured off into a beaker and allowed to settle by themselves, as small particles of copper may accidentally be contained in them; if so, they must be washed clean and added to the platinum dish. Air should not be admitted to the metallic copper while the acid is present, to any great extent. When the washings no longer affect litmus paper, the dish should be placed in an air bath, heated to 100° or 110° C., and dried till the weight is constant—the increase in weight is pure copper. A water-bath may be used for drying the copper, in any case it is preferable to wash it first with strong alcohol.

Instead of a platinum dish porcelain or glass will answer, but more time is required, as there is no galvanic action to hasten the decomposition as with the platinum; in this case the deposited copper is not attached to the sides or bottom of the vessel. See also § 44. 8.

2. Reduction by Grape Sugar and subsequent titration with Ferric Chloride and Permanganate, (Schwarz.)

This process is based upon the fact that grape sugar precipitates cuprous oxide from an alkaline solution of the metal containing tartaric acid; the oxide so obtained is collected and mixed with ferric chloride and hydrochloric acid—the result is the following decomposition:—

$$Cu^2O + Fe^2Cl^6 + 2HCl = 2CuCl^2 + 2FeCl^2 + H^2O$$

Each equivalent of copper reduces one equivalent of ferric to ferrous chloride, which is estimated by permanganate with due precaution. The iron so obtained is calculated into copper by the requisite factor.

The Analytical process: The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or flask, and most of the acid in excess saturated with sodic carbonate; neutral potassic tartrate is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue fluid by adding caustic potash or soda in excess; the vessel is next heated cautiously to about 50° C., in the water-bath, and sufficient grape, milk, or starch sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the heat must never exceed 90° C. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterwards the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is well washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of ferric chloride (free from nitric acid or free chlorine) added, together with a little sulphuric acid; the whole is then warmed and stirred until the cuprous chloride is all dissolved. It is then filtered into a good sized flask, the old and new filters being both well washed with hot water, to which at first, a little free sulphuric acid should be added in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way; bichromate may also be used, but the end of the reaction is not so distinct as usual, from the turbidity produced by the presence of copper.

3. Reduction by Zinc and subsequent titration with Ferric Chloride and Permanganate, (Fleitmann.)

The metallic solution, free from nitric acid, bismuth, or lead, is precipitated with zinc as in § 44. 1 or 44. 8; the copper collected, washed, and dissolved in a mixture of ferric chloride and hydrochloric acid; a little sodic carbonate may be added to expel the atmospheric air. The reaction is—

$$Cu + Fe^2Cl^6 = CuCl^2 + 2FeCl^2.$$

When the copper is all dissolved, the solution is diluted and titrated with permanganate; 56 of iron represent 31·7 of copper.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration; the zinc must be finely divided and the mixture warmed; the copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water then with weak hydrochloric or sulphuric acid and water, to remove the zinc; again with water, and then dissolved in the acid and ferric chloride as before.

4. Estimation as Cupric Iodide, (De Haen and E. O. Brown,) results accurate in the absence of persalts of iron and other reducible substances.

The solution of the metal, if it contain nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralised with sodic carbonate and acetic acid added; the sulphat solution must be neutral, or only faintly acid; excess of acetic aci is of no consequence.

The process is based on the fact that when potassic iodide i mixed with a salt of copper in solution, cupric iodide is precipitate as a dirty white powder, and iodine set free. If the latter is the titrated with hyposulphite and starch liquor, the correspondin quantity of copper is found by the systematic factor.

The Analytical process: The solution (containing not less tha 1 gm. of Cu to each 100 c.c.), free from iron, chlorine or free nitric o hydrochloric acids is brought into a beaker or flask, potassic iodid in good quantity added, and the hyposulphite delivered from a burett till the brown colour has disappeared; starch liquor is then added and $\frac{N}{10}$ iodine, to ascertain the excess of hyposulphite, or the titratio may proceed direct by adding starch at first, and then hyposulphit till the blue colour is discharged.

Example: 10 c.c. of solution of cupric sulphate, containin 0·39356 gm. = 0·1 gm. of copper was mixed with potassic iodide in beaker, and 19 c.c. of $\frac{N}{10}$ hyposulphite added, then starch liquo and 3·2 c.c. of $\frac{N}{10}$ iodine required to produce the blue colour = 15· c.c. of hyposulphite; this multiplied by 0·00635 gave 0·1003 gm of copper instead of 0·1 gm.

In order to remove iron from copper solutions, previous to thei analysis, it has been recommended to precipitate it with ammoni on the one hand, or to boil with sodic acetate and precipitate a basic acetate on the other. In neither case can very satisfactor results be obtained, for with ammonia at least three precipitation are necessary to remove all the copper from the ferric oxide; boilin with sodic acetate does not always separate all the iron, and even i it should do so, the precipitate holds the copper tenaciously; th collection of fluid therefore, by these repeated precipitations an washings, is so considerable, that the process cannot be applied except after evaporation to a small bulk. The sodic acetate is fa preferable to the ammonia; it must, however, be used in larg quantity, and the precipitate washed with hot water containin sodic acetate. In certain cases (*i.e.*, where metals may be presen which would interfere with the titration of the entire liquid b Parkes' process, § 44. 5), it may be advisable to precipitat the iron by ammonia, slightly wash the precipitate, and the break the filter and wash it through the funnel into a whit capsule, and titrate with potassic cyanide at once for the sligh amount of copper present, adding the weight so found to tha obtained in the filtrate by some other method.

6. Estimation by Potassic Cyanide, (Parkes and C. Mohr,) results tolerably accurate, in the absence of manganese, nickel, cobalt, mercury, and silver.

This well-known and much used process for estimating copper depends upon the decoloration of an ammoniacal solution of copper by potassic cyanide; the reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, ammonic cyanide and formate, (Liebig). Owing to the influence exercised by variable quantities of ammonia, or its neutral salts, upon the decoloration of a copper solution by the cyanide, it is necessary that the solution analysed should contain pretty nearly the same proportion of ammonia as that upon which the cyanide has been originally titrated, and no heat should be used. See also § 44.8.

Examples: 1. 10 c.c. of solution of cupric sulphate, containing 0·10 gm. of Cu, with 1 c.c. of ammonia, spec. grav. 0·900, required 21·3 c.c. of cyanide solution.

2. 50 c.c. of copper solution = 0·50 gm. of Cu, and 5 c.c. of ammonia, require 106·5 c.c. of cyanide.

These agree exactly.

3. 20 c.c. of copper solution = 0·20 gm of Cu, with 6 c.c. of ammonia, require 43 c.c. of cyanide instead of 42·6.

4. 20 c.c. of copper = 0·20 gm. of Cu, with 20 c.c. of ammonia, required 43 c.c. of cyanide, instead of 42·6.

The results with salts of ammonia were very similar, but even more marked.

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field, however, has stated that this is not necessary ("Chem. News," vol. 1. p. 25), and I can fully endorse his statement that the presence of the suspended ferric oxide is no hindrance to the estimation of the copper, in fact it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange brown; if it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary, to enable the operator to hit the exact point, and it is always well to make use of both indicators. The following experiment is given from among many others.

10 c.c. of copper solution = 0·10 gm. of Cu, were put into a small white porcelain dish, and 2 c.c. of ammonia, 0·900 added, then the

cyanide cautiously delivered from the burette, till the faintes violet tinge only was perceptible, the quantity so used was 21·3 c.c. 10 c.c. of copper solution were then put into another dish, a littl freshly precipitated ferric oxide added, together with 2 c.c. o ammonia. The cyanide was then delivered without looking at th burette until the oxide had acquired the proper colour; the burett was found to stand at 21·3 c.c., and the clear solution possessed the same faint tint as before.

The solution of potassic cyanide should be titrated afresh at intervals of a few days. Further details of this process are given, § 44.8.

6. Estimation as Sulphide, (Pelouse,) results tolerably accurate in the absence of tin, nickel, cobalt, or silver.

It is first necessary to have a solution of pure copper, of known strength, which is best made by dissolving 39·291 gm. of pure cupric sulphate in 1 litre of distilled water; each c.c. will contain 0·01 gm. of pure metallic copper.

Precipitation in Alkaline Solution. This process is based on the fact that if an ammoniacal solution of copper is heated to from 40° to 80° C., and a solution of sodic sulphide added, the whole of the copper is precipitated as oxysulphide, leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point; special practice, however, will enable the operator to hit the exact point closely.

Example: A measured quantity, say 50 c.c., of standard solution of copper, is freely supersaturated with caustic ammonia, and heated till it begins to boil; the temperature will not be higher than 80° C. in consequence of the presence of the ammonia; it is always well, however, to use a thermometer; the sodic sulphide is delivered cautiously from a Mohr's burette, until the last traces of blue colour have disappeared from the clear liquid above the precipitate. The experiment is repeated, and if the same result is obtained, the number of c.c. or dm. required to precipitate the amount of copper contained in 50 c.c. or dm., = 0·5 gm. or 5 grn. respectively, is marked upon the alkaline sulphide bottle. As the strength of the solution gradually deteriorates, it must be titrated afresh every day or two. Special regard must be had to the temperature of the precipitation, otherwise the accuracy of the process is seriously interfered with.

Precipitation in Acid Solution. The copper solution is placed in a tall stoppered flask of tolerable size (400 or 500 c.c.), freely acidified with hydrochloric acid, then diluted with about 200 c.c. of hot water.

The alkaline sulphide is then delivered in from a burette, the stopper replaced, and the mixture well shaken; the precipitate of copper sulphide settles readily leaving the supernatant liquid clear, fresh sulphide solution is then at intervals added until no more precipitate occurs. The calculation is the same as in the case of alkaline precipitation, but the copper is precipitated as pure sulphide instead of oxysulphide.

7. Estimation by Stannous Chloride and Permanganate—(Weil.)

This process is based on the fact, that a solution of a cupric salt in excess of hydrochloric acid at a boiling heat, shows, even when the smallest trace is present, a greenish yellow colour. If to such a solution stannous chloride is added in excess, a colourless cuprous chloride is produced, and the loss of colour indicates the end of the process.

$$2CuCl^2 + SnCl^2 = Cu^2Cl^2 + SnCl^4$$

The change is easily distinguishable to the eye, but should any doubt exist as to whether stannous chloride is in excess a small portion of the solution may be tested with mercuric chloride, any precipitate of calomel indicates the presence of stannous chloride.

The tin solution is prepared as described in § 31. 3.

A standard copper solution is made by dissolving pure cupric sulphate in distilled water, in the proportion of 15·734 gm. per litre = 4 gm. of Cu.

Process for copper alone: 25 c.c. of the copper solution= 0·1 gm. of Cu is put into a white glass flask, 5 c.c. of pure strong hydrochloric acid added placed on a sand bath and brought to boiling heat, the tin solution is then quickly delivered in from a burette until the colour is nearly destroyed, finally a drop at a time till perfectly so; 5 c.c. more of acid is then added, and should this produce any return of colour, more tin solution is required to remove it. The liquid should be as colourless as distilled water, but if any doubt exist, it is better to test a portion of the cooled liquid with a few drops of solution of mercuric chloride; if no faint precipitate of calomel is produced, sufficient stannous chloride has not been used.

A sample of copper ore is prepared in the usual way by treatment with nitric acid, and afterwards with sulphuric or hydrochloric acid to remove the nitric. Silica, lead, tin, antimony, silver, or arsenic, are of no consequence, as when the solution is diluted with water to a definite volume, the precipitates of these substances settle to the bottom of the measuring flask, and the clear liquid may be taken out for titration.

Process for ores containing copper and iron: In the case of copper ores where iron is also present, the quantity of tin solution required will of course represent both the iron and the copper; in this case a second titration of the original solution is made with permanganate, and the quantity so found is deducted from the total quantity; the amount of tin solution corresponding to copper is thus found.

Example: A solution was prepared from 4 gm. of ore and diluted to 250 c.c., 25 c.c. required 26·75 c.c. of tin solution whose strength was 16·2 c.c. for 0·1 gm. of Cu.

25 c.c. of ore solution were diluted, warmed, zinc and platinum added till reduction was complete, and titrated with permanganate whose quantity = 0·0809 gm. of Fe.

The relative strength of the tin solution to iron is 18·34 c.c. = 0·1 gm. of Fe: thus—

$$\begin{array}{ccccc} \text{eq. wt. Cu} & : & \text{eq. wt. Fe} = \text{Cu} & : & x\ \text{Fe} \\ 63{\cdot}5 & & 56 = 0{\cdot}1 & : & 0{\cdot}0883 \end{array}$$

therefore 0·1 gm. of Cu = 0·0883 gm. of Fe = 16·2 c.c. of $SnCl^2$

whence 0·0883 : 0·1 = 16·2 : 18·34

thus 0·0809 Fe (found above) = 14·837 of c.c. $SnCl^2$

0·1 : 0·0809 = 18·34 : 14·837 hence

Iron and copper	=	26·750 c.c. $SnCl^2$
Subtract for iron	=	14·837
Leaving for copper		11·913

25 c.c. of ore solution therefore contained 16·2 : 0·1 = 11·913 : 0·0735 gm. of Cu, and as 4 gm. of ore = 250 c.c. contained of course 0·735 gm. of Cu = 18·38% Cu. Analysis by weight as a control gave 18·34% Cu.

Fe volumetrically 20·25% by weight 20·10%.

Process for ores containing nickel or cobalt: The ore is dissolved in nitric or nitro-hydrochloric acid, then nearly neutralized with sodic carbonate, diluted with cold water, and freshly precipitated baric carbonate and some ammonic chloride added; the whole is well mixed together, producing a precipitate containing all the copper and iron, while the nickel or cobalt remains in solution; the precipitate is first washed by decantation, collected on a filter, well washed, then dissolved in hydrochloric acid, and titrated with stannous chloride as before described.

8. Technical Examination of Copper Ores. (Steinbeck's Process.)

In May 1867 the Directors of the Mansfield Copper Mines offered a premium for the best method of examining these ores, the chief conditions being tolerable accuracy, simplicity of working, and the possibility of one operator making at least eighteen assays in the day.

The fortunate competitor was Dr. Steinbeck, whose process satisfied completely the requirements of the Directors. The whole report is contained in Fresenius' "Zeitschrift," part i, 1869, and is also translated in "Chem. News," April 16, 1869. The following is a somewhat condensed *resumé* of the process, the final titration of the copper being accomplished by potassic cyanide as in § 44.5. A very convenient arrangement for filling the burette with standard solution where a series of analyses have to be made, and the burette continually emptied is shown in fig. 31; it may be refilled by simply blowing upon the surface of the liquid.

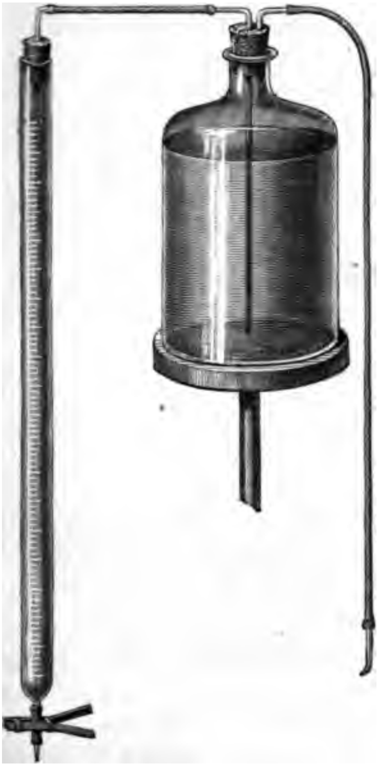

Fig. 31.

(*a*.) **The extraction of the Copper from the Ore.** 5 gm. of pulverised ore are put into a flask with from 40 to 50 c.c. of crude hydrochloric acid, specific gravity 1·16, whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After a while there is added to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a sand bath for half an hour, and the contents boiled for about fifteen minutes, after which the whole of the copper occurring in the ore, and all other metals are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or to contain at the most only 0·01 to 0·03 per cent.

(*b.*) **Separation of the Copper.** The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker glass of about 400 c.c. capacity; in this beaker a rod of metallic zinc, weighing about 50 gms., has been previously placed, fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate should not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is, owing especially also to the entire absence of nitric acid, completely finished in from half to three quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace of copper can or should be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must always be employed) has been removed, the metal is repeatedly and carefully washed by decantation with fresh water, and care taken to collect together every particle of the spongy mass.

(*c.*) **Quantitative estimation of the precipitated copper.** To the spongy metallic mass in the beaker glass, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper dissolved by the aid of moderate heat, in the form of cupric nitrate, which, in the event of any small quantity of lead being present, will of course be contaminated with lead.

When copper ores are dealt with, which contain above 6 per cent. of copper, which may be approximately estimated from the bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are applied for dissolving the metal. The solution thus obtained is left to cool, and next mixed, immediately before titration with potassic cyanide, with 10 c.c. of normal solution of liquid ammonia, prepared by diluting 1 volume of liquid ammonia, sp. gr. 0·93, with 2 volumes of distilled water. The titration with cyanide is conducted as described in § 44.5.

In the case of such ores as yield over 6 per cent. of copper, and when a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then exactly divided into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue coloured solution only contains in addition to the copper compound, ammonic nitrate; any lead which might have been dissolved having been precipitated as hydrated oxide, which does not interfere with the titration with cyanide. The solution of the last-named salt is so arranged, that 1 c.c. thereof exactly indicates 0·005 gm. of copper. Since, for every assay, 5 gms. of ore have been taken, 1 c.c. of the titration fluid is equal to 0·1 per cent. of copper, according to the following proportion:—

$$5 : 0{\cdot}005 :: 100 : x = 0{\cdot}1$$

it hence follows that, by multiplying the number of c.c. of cyanide solution used to make the blue colour of the copper solution disappear by 0·1, the percentage of copper contained in the ore is immediately ascertained.

Steinbeck tested this method specially, in order to see what influence is exercised thereupon by (1) ammonic nitrate; (2) caustic ammonia, (3) lead. The copper used for the experiments for this purpose was pure metal, obtained by galvanic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. 5 gms. of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of normal nitric acid, the flask gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. 30 c.c. of this solution were always applied to titrate one and the same solution of potassic cyanide under all circumstances. When 5 gms. of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·150 gm. of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 gms. of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of normal nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

The influence of double quantities of ammonic nitrate and free caustic ammonia (the quantity of copper remaining the same), is shown as follows :—

(*a.*) 30 c.c. of the normal solution of copper, containing exactly 0·150 gm. of copper, were rendered alkaline with 10 c.c. of normal ammonia, and were found to require, for entire decoloration, 29·8 c.c. of cyanide solution; a second experiment, again with 30 c.c. of normal copper solution, and otherwise, under identically the same conditions, required 29·9 c.c. of cyanide solution. The average is 29·85 c.c.

(*b.*) When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia, instead of only 8, whereby the quantity of free ammonia and of ammonic nitrate is made double what it was in the case of *a*, there is required of the same cyanide solution 30·3 c.c. to produce decoloration. A repetition of the experiment, exactly under the same conditions, gave 30·4 c.c. of the cyanide solution employed; the average is, therefore, 30·35 c.c.—the difference amounts to only 0·05 per cent. of copper which may be allowed for in the final calculation.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of cyanide, and especially when ammonic carbonate, sulphate, and, worse still, chloride are simultaneously present, these salts exert a very disturbing influence, see § 44.5. The presence of lead in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness with the blue tint; but this does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Steinbeck purposely made some experiments to test this point, and his results show that a moderate quantity of lead has no influence.

Experiments were also carefully made to ascertain the influence of zinc, the result of which showed that up to 5 per cent. of the copper present, the zinc had no disturbing action, but a considerable variation occurred as the percentage increased above the proportion. Care must therefore always be taken in washing the spongy copper precipitated from the ore solution by means of zinc.

The titration must always take place at ordinary temperatures, since heating the ammoniacal solution while under titration to 40°, or 45°C, considerably reduces the quantity of cyanide required.

9. Estimation of Copper by Colour Titration.

This method can be adopted with very accurate results, as in the case of iron § 42. 7, and is available for slags, poor cupreous pyrites, waters, &c. (See Carnelly, Chem. News, Dec. 31, 1875).

The reagent used is the same as in the case of iron, viz., potassic ferrocyanide, which gives a purple-brown colour with very dilute solutions of copper. This reaction, however, is not so delicate as it is with iron, for 1 part of the latter in 13,000,000 parts of water can be detected by means of potassic ferrocyanide, while 1 part of copper in a neutral solution, containing ammonic nitrate, can only be detected in 2,500,000 parts of water. Of the coloured reactions which copper gives with different reagents, those with sulphuretted hydrogen and potassic ferrocyanide are by far the most delicate, both shewing their respective colours in 2,500,000 parts of water.

Of the two reagents sulphuretted hydrogen is the more delicate, but potassic ferrocyanide has a decided advantage over sulphuretted hydrogen in the fact that lead, when not present in too large quantity, does not interfere with the depth of colour obtained, whereas to sulphuretted hydrogen it is, as is well known, very sensitive.

And though iron if present would, without special precaution being taken, prevent the determination of copper by means of potassic ferrocyanide, yet by the method as described below, the amounts of these metals contained together in a solution can be estimated by this reagent.

Ammonic nitrate renders the reaction much more delicate ; other salts, as ammonic chloride and potassic nitrate, have likewise the same effect.

The method of analysis consists in the comparison of the purple-brown colours produced by adding to a solution of potassic ferrocyanide—first, a solution of copper of known strength, and secondly the solution in which the copper is to be determined.

The solutions and materials required are as follows:—

(1.) Standard copper solution.—Prepared by dissolving 0·393 gm. of pure $CuSO^4, 5H^2O$ in one litre of water. 1 c.c. is then equivalent to 0·1 m.gm. Cu.

(2.) Solution of ammonic nitrate.—Made by dissolving 100 gm. of the salt in one litre of water.

(3.) Potassic ferrocyanide solution.—Containing 1 part of the salt in 25 parts of water.

(4.) Two glass cylinders holding rather more than 150 c.c. each, the point equivalent to that volume being marked on the glass. They must, of course, both be of the same tint and as nearly colourless as possible.

A burette, graduated to $\frac{1}{10}$ c.c. for the copper solution: a 5 c.c. pipette for the ammonic nitrate, and a small tube to deliver the potassic ferrocyanide in drops.

The Analytical process: Five drops of the potassic ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined into one of them, and both filled up to the mark with distilled water, 5 c.c. of the ammonic nitrate solution added to each, and then the standard copper solution ran gradually into the other, till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of c.c. used are then read off. Each c.c. corresponds to 0·1 m.gm. of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be estimated must be neutral, for if it contain free acid the latter lessens the depth of colour and changes it from a purple-brown to an earthy brown. If it should be acid it is rendered slightly alkaline with ammonia, and the excess of the latter got rid of by boiling. The solution must not be alkaline, as the brown coloration is soluble in ammonia and decomposed by potash or soda; if it be alkaline from ammonia this is remedied as before by boiling it off; while free potash or soda, should they be present, are neutralised by an acid and the latter by ammonia.

Within moderate limits the amount of potassic ferrocyanide does not affect the accuracy of the method, as was proved by several experiments; for instance, when ½ c.c. and 2 c.c. of the ferrocyanide were added to the two cylinders respectively, water up to the mark, and 5 c.c. of ammonic nitrate, 7 c.c. of the standard copper solution produced in each an equal depth of colour.

The same may be said of the ammonic nitrate, for in one of several trials, all leading to the same result, there were five drops of ferrocyanide in each cylinder, with water up to the mark, 5 c.c. of ammonic nitrate in one and 15 c.c. in the other, when an equal depth of colour was obtained on running into each 7 c.c. of the standard copper solution.

The results obtained are fairly uniform, and will compare with any other process which can be used for the estimation of minute quantities of copper.

Experiment proved that colourless salts of the alkaline and earthy metals, as also organic matter like sugar, had no effect on the colour.

Lead when present in not too large quantity has little or no effect on the accuracy of the method. The precipitate obtained on adding potassic ferrocyanide to a lead salt is white, and this, except when present in comparatively large quantity with respect to the copper, does not interfere with the comparison of the colours.

When copper is to be estimated in a solution containing iron the following is the method of procedure to be adopted. A few drops of nitric acid are added to the solution in order to oxidise the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present this can be done easily and completely if there be only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid and re-precipitated by ammonia, filtered, and washed. The iron precipitate is now free from copper, and in it the iron can be estimated by dissolving in nitric acid, making the solution nearly neutral with ammonia and determining the iron by the method in § 42, 7. The filtrate from the iron precipitate is boiled till all the ammonia is completely driven off, and the copper estimated in the solution so obtained as already described.

When the solution containing copper is too dilute to give any coloration directly with potassic ferrocyanide, a measured quantity of it must be evaporated to a small bulk and filtered if necessary, and if it contain iron, also treated as already described.

In the determination of copper and iron in water, for which the method is specially applicable, a measured quantity is evaporated to dryness, with a few drops of nitric acid ignited to get rid of any organic matter that might colour the liquid, and dissolved in a little boiling water and a drop or two of nitric acid, if it is not all soluble it does not matter; ammonia is next added to precipitate the iron, the latter filtered off, washed, re-dissolved in nitric acid, and again precipitated by ammonia, filtered off, and washed. The filtrate is added to the one previously obtained, the iron estimated in the precipitate and the copper in the united filtrates.

ZINC.

$Zn = 65$.

1 c.c. $\frac{N}{10}$ solution = 0·00325 gm. Zinc.
Metallic iron × 0·5809 = Zinc.
" × 0·724 = Zinc oxide.
Double iron salt × 0·08298 = Zinc.
" " × 0·1034 = Zinc oxide.

1. By Iodine, results accurate in the absence of Manganese and the heavy metals in general. (C. Mohr.)

§ 45. In the analysis of potassic ferricyanide, by Lenssen's method, § 66, it is shown that greater exactness may be obtained through the use of an excess of zinc in the mixture, so that the iodine liberated shall be the true measure of the substance.

In the present method the process may be considered to be reversed:—with an excess of ferricyanide the liberated iodine shall express the quantity of zinc sought.

If to a solution of zinc in acetic acid an excess of potassic ferricyanide is added, a reddish yellow precipitate of zinc ferricyanide occurs, having the composition, $Zn^3(Fe^2Cy^6)^2$.

If now to this mixture an excess of potassic iodide be added, the decomposition occurs as follows. $2Zn^3(Cy^6Fe)^2 + 4H\bar{A} + 4KI = 3Zn^2Cy^6Fe + 4K\bar{A} + H^4Cy^6Fe + I^4$. Thus 2 eq. I = 3 eq. Zn, therefore 1 c.c. of $\frac{N}{10}$ hyposulphite = 0·00975 gm. of zinc.

The Analytical process: The metal and its compounds must exist in an acetic acid solution, which is best managed by dissolving the ores in *aqua regia*, evaporating to dissipate the excess of acid, neutralising the remainder with sodic carbonate, then adding a strong solution of sodic acetate in excess, and boiling to precipitate the iron; allow to subside and decant, re-precipitate and boil, then filter and wash with boiling water containing a little sodic acetate; iron, but not manganese, is removed by this means so that should the latter be present, the process will not be applicable. In the presence of other metals the zinc must be separated as sulphide or oxide, and afterward brought into solution in acetic acid.

To the acetic acid solution so prepared a freshly-made solution of potassic ferricyanide is added in slight excess, (known by a drop of the mixture giving a blue colour with ferrous salts), potassic iodide in sufficient quantity is then added, together with starch liquor, and the titration with $\frac{N}{10}$ hyposulphite performed as usual—the greenish blue colour of the mixture entirely disappears, and gives place to the pure reddish yellow of potassic ferricyanide, when in solution.

Fr. and C. Mohr and Fresenius have found the method tolerably reliable. I have also found the same with pure zinc salts, it is not necessary, therefore, to give examples further than to say that in the case of pure salts of zinc 99·8 and 100·12 were obtained instead of 100,—it is doubtful if the process is worth much in treating impure ores of zinc.

2. Precipitation as Sulphide and subsequent titration with Ferric Salts and Permanganate. (Schwarz.)

The principle of this method is based on the fact that when zinc sulphide is mixed with ferric chloride and hydrochloric acid, or better still, with ferric sulphate and sulphuric acid, ferrous or zinc chloride, or sulphates respectively, and free sulphur are produced: if the ferrous salt so produced is estimated with permanganate or bichromate, the proportional quantity of zinc present is ascertained, 2 eq. Fe. represent 1 eq. Zn.

The Analytical process: Ores of zinc are treated with hydrochloric, or in the case of blende, with that and nitric acid, dissolved, evaporated to dissipate excess of acid, and then precipitated with a mixture of carbonate of and caustic ammonia, and digested warm till all the zinc precipitate is dissolved, the residue is washed with ammoniacal water and the filtrate and washings mixed. This ammoniacal solution (which should contain all the zinc), is then heated, and the zinc precipitated in a tall beaker, with a slight excess of sodic or ammonic sulphide, then covered closely with a glass plate, and set aside in a warm place for a few hours. The clear liquid is removed by a syphon, and hot water containing some ammonia again poured over the precipitate, allowed to settle, and again removed, and the washing by decantation repeated three or four times; finally the precipitate is brought upon a tolerably large and porous filter, and well washed with warm water containing ammonia, till the washings no longer discolour an alkaline lead solution. Bunsen's filter pump may be used here with great advantage.

The filter with its contents is then pushed through the funnel into a large flask containing a sufficient quantity of ferric sulphate mixed with sulphuric acid, immediately well stopped or corked, gently shaken, and put into a warm place; after some time it should be again well shaken, and set aside quietly for about ten minutes. After the action is all over the mixture should possess a yellow colour from the presence of undecomposed ferric salt; when the cork or stopper is lifted there should be no odour of sulphuretted hydrogen. The flask is then nearly filled with cold distilled water, if necessary some dilute sulphuric acid added, and the contents of the flask titrated with permanganate or bichromate as usual. The free sulphur and filter will have no reducing effect upon the permanganate if the solution be cool and very dilute.

Example: 1 gm. of pure zinc oxide was dissolved in hydrochloric acid, supersaturated with ammonic sulphide, the precipitate well washed and digested with acid ferric sulphate, the whole diluted to 500 c.c. in a stoppered flask, and 100 c.c. titrated with permanganate of such strength that 120 c.c. = 1 gm. iron. 33·4 c.c. were required = 0·278 gm. of iron, this multiplied by 5, as $\frac{1}{5}$ only was taken, gave 1·390 gm. of iron, which multiplied by 0·724, the factor for zinc oxide, gave 1·0063 gm. instead of 1 gm.

3. Precipitation by Standard Sodic Sulphide, with Alkaline Lead Solution as Indicator, applicable to most Zinc Ores and Products.

The ammoniacal solution of zinc is prepared just as previously described in Schwarz's method.

The standard sodic sulphide is best made by saturating a portion of caustic soda solution with sulphuretted hydrogen, then adding sufficient soda solution to remove the odour of the free gas, and diluting the whole to a convenient strength for titrating.

The standard zinc solution is best made by dissolving 44·12 gm. of pure zinc sulphate to the litre; 1 c.c. will then contain 0·010 gm. of metallic zinc, and upon this solution, or one prepared from pure metallic zinc of the same strength, the sulphide solution must be titrated.

The alkaline lead solution used as indicator is made by heating together acetate of lead, tartaric acid, and caustic soda solution in excess until a clear solution is produced. It is preferable to mix the tartaric acid and soda solution first, so as to produce sodic tar-e, or if the latter salt is at hand, it may be used instead of aric acid: some operators use sodic nitroprusside instead of l.

he Analytical process: 50 c.c. of zinc solution = 0·5 gm. Zn put into a beaker, a mixture of solutions of ammonia and ionic carbonate (3 of the former to about 1 of the latter) d in sufficient quantity to redissolve the precipitate which first s. A few drops of the lead solution are then by means of a rod placed at some distance from each other, on filtering paper, upon a slab or plate.

ie solution of sodic sulphide contained in an ordinary Mohr's te is then suffered to flow into the zinc solution until, on ing a drop from the mixture and placing it upon the filtering r so that it may expand and run into the drop of lead solution, ck line occurs at the point of contact; the reaction is very ate; at first it will be difficult, probably, to hit the exact , but a second trial with 25 or 50 c.c. of zinc solution will le the operator to be certain of the corresponding strength of ulphide solution. As this latter is always undergoing a slight ge, it is necessary to titrate occasionally.

rect titration with pure zinc solution gave 99·6 and 100·2, ad of 100.

oll recommends the use of protochloride of nickel as indicator, ad of sodic nitroprusside or lead. The drops are allowed w together on a porcelain plate; while the point of contact s a blue or green colour the zinc is not all precipitated by the sulphide, therefore the latter must be added until a grayish colour appears at contact.

nother indicator is paper soaked in a nearly neutral dilute ion of cobaltous chloride, which when dry and cold is rless; when touched with a drop of liquid containing sodic ide, it turns to a green tint, rapidly becoming brown when ed.

stimation as Ferrocyanide in Acetic Acid Solution (Galetti).

hen ores containing zinc and iron are dissolved in acid, he iron precipitated with ammonia, the ferric oxide invariably s down with it a portion of zinc, and it is only by repeated pitation that the complete separation can be made. In this ss the zinc is converted into soluble acetate and titrated by a ard solution of potassic ferrocyanide in the presence of ble ferric acetate.

e standard solution of potassic ferrocyanide, as used by

Galetti, contains 41·250 gm. per litre, therefore 1 c.c. = 0·01 gm. of Zn, but its actual working power must be fixed by experiment.

The standard zinc solution contains 10 gm. of pure metallic zinc per litre dissolved in hydrochloric acid.

The process is available in the presence of moderate quantities of iron and lead, but copper, manganese, nickel, and cobalt, must be absent, or previously removed.

The adjustment of the ferrocyanide solution must be made in precisely the same way, and with the same volume of liquid as the actual analysis of ores, and is best done as follows:

25 c.c. of zinc solution are measured into a beaker, 15 c.c. of liquid ammonia of sp. gr. 0·900 added to render the solution alkaline, then very cautiously acidified with acetic acid, and 50 c.c. of acid ammonic acetate (made by adding together of 20 c.c. ammonia of sp. gr. 0·900, 15 c.c. of concentrated acetic acid and 65 c.c. of distilled water) which is poured into the mixture, then diluted to 250 c.c., and warmed to about 50° C. The titration is then made with the ferrocyanide solution by adding it from a burette until the whole of the zinc is precipitated. Galetti judges the ending of the process from the first change of colour from white to ash grey, which occurs when the ferrocyanide is in excess, but I prefer to ascertain the ending by taking drops from the solution, and bringing them in contact with solution of uranic acetate or nitrate on a white plate until a faint brown colour appears. The ferrocyanide solution should be of such strength that measure for measure it agrees with the standard zinc solution—in the present case 25 c.c. would be required.

In examining ores of zinc, such as calamine and blende, Galetti always takes 0·5 gm. for the analysis, and makes the solution up to 500 c.c. Calamine is at once treated with hydrochloric acid in sufficient quantity to bring it into solution; blende is treated with *aqua regia*, and evaporated with excess of hydrochloric acid to remove nitric acid; the solutions of zinc so obtained invariably contain iron, which together with the zinc is kept in solution by the hydrochloric acid, but to insure the peroxidation of the iron, it is always advisable to add a little potassic chlorate at a boiling heat during the extraction of the ore. The hydrochloric solution is then diluted to about 100 c.c. with water, 30 c.c. of ammonia added, heated to boiling, exactly neutralized with acetic acid, 100 c.c. of the acid ammonic acetate just described poured in, and diluted to about 500 c.c. The mixture as prepared will contain all the zinc in solution, and the iron will be precipitated as acetate; the titration may at once be proceeded with at a temperature of about 50° to 60° C. by adding the ferrocyanide until the necessary reaction with uranium is obtained. As before mentioned Galetti takes the change of colour as the ending of the process, and when iron is present this is quite distinguishable, but it requires considerable practice to rely upon, and it is therefore safer to use the uranium indicator. When using the uranium, however, I prefer to dilute the zinc solution less, both in the adjustment of the standard ferrocyanide and the analysis of ores. The dilution is necessary with Galetti's method of ending the process, but half the volume of liquid or even less, is better with the external indicator.

5. Estimation as Ferrocyanide in Hydrochloric Acid Solution, (Fahlberg and Maxwell Lyte.)

This method is not available in the presence of iron, copper, ickel, or cobalt, but lead, manganese, and alumina do not interfere.

The standard solution of ferrocyanide is made of such strength, hat 1 c.c.=0·01 gm. of Zinc. Lyte finds that this is obtained by issolving 43·2 gm. of pure potassic ferrocyanide and diluting to litre; this corresponds volume for volume with a solution of 0 gm. of pure zinc in excess of hydrochloric acid diluted to 1 litre. y experiments confirm this, but each operator is advised to djust his solutions by experiment, always using the same quanities of reagents and volume of liquid; the end of the reaction etween the zinc and ferrocyanide is found by uranium.

The Analytical process. If a solution of zinc freely acidified ith hydrochloric acid is heated to near the boiling point, two or hree drops of uranic solution added, and the ferrocyanide elivered into the mixture from a burette, white zinc ferrocyanide mmediately precipitates, and as the drops of ferrocyanide fall nto the mixture, a brown spot of uranic ferrocyanide appears ut disappears again on stirring so long as free zinc exists n solution; the moment all the zinc is converted into ferrocyanide, he addition of test solution tinges the whole liquid brown. This addition of uranium to the liquid may be used as a guide o the final testing on a porcelain plate, since as the precipitation pproaches completion, the tinge of brown disappears more slowly; he actual ending, however, is always ascertained by spreading a rop or two of the liquid upon the plate, bringing into contact with t a glass rod moistened with uranic solution; when the same shade f colour is produced as occurred in the original titration of the errocyanide solution the process is ended.

Lyte gives the following method of treating a blende containing ead, copper, and iron, (Chem. News, vol. xxi, p. 222.)

Example: 2 gm. of finely powdered ore were boiled with strong ydrochloric acid and a little potassic chlorate, the insoluble atter again treated in like manner, the solutions mixed and evaporated somewhat, washed into a beaker, cooled, and moist baric carbonate added to precipitate iron, allowed to stand a few hours, then filtered into a 200 c.c. flask containing 10 c.c. of strong HCl, and washed until the exact measure was obtained. 20 c.c. =0·2 gm. of blende were measured into a small beaker, diluted with the same quantity of water, 3 drops of uranic solution added, and the ferrocyanide delivered in from a burette; when 70 c.c. were added the brown tinge disappeared slowly; the testing on a white plate was then resorted to, and the ferrocyanide added drop by drop until the proper effect occurred at 73 c.c. As a slight excess of ferrocyanide was necessary to produce the brown colour, 0·2 c.c. was deducted, leaving 72·8 c.c. as the quantity necessary to precipitate all the zinc; the 0·2 gm. of blende therefore contained 0·0728 gm. of Zn or 36·4 per cent.

The sample in question contained about 2·7°/₀ of copper, but this was precipitated with the iron by the baric carbonate; had it contained a larger quantity, the process would not have been available unless the copper was removed by other means.

Fahlberg (Zeitshrift für An. Chem. 1874, 379) estimates the zinc in hydrochloric solution with ferrocyanide and uranic indicator, but recommends the addition of ammonic chloride to the extent of about five times the weight of zinc present.

The standard ferrocyanide must of course be adjusted in the same way as in the analysis of ores, and it must not be forgotten that the presence of ammoniacal salt in quantity affects the production of colour with uranium, so that it is absolutely necessary to work with the same quantities of reagents and volume of liquid in all cases.

Ores containing galena or copper are treated with *aqua regia*, then boiled with excess of hydrochloric acid, the heavy sulphides precipitated with sulphuretted hydrogen and filtered off, the iron peroxidised with nitric acid or potassic chlorate, cooled, precipitated with ammonia, and the precipitate dissolved and re-precipitated twice to remove all zinc; the ammoniacal solutions are then mixed, neutralized with hydrochloric acid, 10 or 15 c.c. of concentrated HCl added, and titrated with ferrocyanide, regardless of the manganese present. Fahlberg states that the process yields good results with zinc ores containing lead, copper, manganese, and iron.

6. Estimation of Zinc as Oxalate.

This method is based on the fact that all the metals of the magnesia group are precipitated in the absence of alkaline salts by oxalic acid, with the addition of alcohol. The cases are very few in which such a method can be made available, but the process as described by W. G. Leison, (Silliman's Journ., Sept., 1870,) is here given.

The zinc compound is obtained, preferably as sulphate, in neutral solution, and strong solution of oxalic acid and a tolerable quantity of strong alcohol are added; zinc oxalate quickly separates in a fine crystalline powder, which when washed by alcohol from excess of oxalic acid and dried, can be dissolved in hot dilute sulphuric acid, and titrated with permanganate; the amount of zinc is calculated from the weight of oxalic acid so found. If the zinc oxalate be washed on a paper filter, it cannot be separated from the paper without contamination with fibres of that material, which would of course affect to some extent the permanganate solution. Hence it is advisable to filter through very clean sand, best done by a special funnel ground conical at the throat; into this is dropped a pear-shaped stopper with a long stem, the pear-shaped stopper fitting the funnel throat tightly enough to prevent sand but not liquids from passing; a layer of sand being placed upon the globular end of the stopper and packed closely, the liquid containing the oxalate is brought upon it and so washed; finally the stopper is lifted, the sand and oxalate washed through with dilute acid into a clean flask, and the titration completed.

MANGANESE.

$Mn = 55$, $MnO = 71$, $MnO^2 = 87$.

Factors.

Potassic ferrocyanide	×	$0{\cdot}0842 = MnO$.
Double iron salt	×	$0{\cdot}0911 = MnO$.
Metallic iron	×	$0{\cdot}7768 = MnO^2$.
Cryst. oxalic acid	×	$0{\cdot}6916 = MnO^2$.
Double iron salt	×	$0{\cdot}111 = MnO^2$.

1 c.c. $\frac{N}{10}$ solution = 0·00355 gm. MnO or = 0·004357 gm. MnO^2.

§ 46. All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid yield chlorine in the following ratios—

$$Mn^2O^3 = 1 \text{ eq. } O = 2 \text{ eq. } Cl.$$
$$Mn^3O^4 = 1 \text{ eq. } O = 2 \text{ eq. } Cl.$$
$$Mn\,O^2 = 1 \text{ eq. } O = 2 \text{ eq. } Cl.$$
$$Mn\,O^3 = 2 \text{ eq. } O = 4 \text{ eq. } Cl.$$
$$Mn^2O^7 = 5 \text{ eq. } O = 10 \text{ eq. } Cl.$$

The chlorine so produced can be allowed to react upon a known weight of ferrous salt, and when the reaction is completed, the unchanged amount of iron salt is found by permanganate or bichromate.

Or, the chlorine may be led by a suitable arrangement into a solution of potassic iodide, there setting free an equivalent quantity of iodine, which is found by the aid of sodic hyposulphite.

Or, in the case of manganese ores, the reaction may take place with oxalic acid, resulting in the production of carbonic acid which can be weighed as in Fresenius and Wills' method, measured as in Parry's method, or the amount of unchanged acid remaining after the action can be found by permanganate.

1. Estimation by reduction of Potassic Ferricyanide, (Lenssen.)

If protoxide or a protosalt of manganese is boiled with an alkaline solution of potassic ferricyanide, the latter becomes converted into ferrocyanide, while the manganese precipitates as hydrated MnO^2. Lenssen found, however, that the oxidation of the precipitate was not uniform, unless at least 1 eq. of ferric oxide was added with every 1 eq. of manganese. The precipitate, under these circumstances, possesses a constant composition. The amount of manganese present is indirectly found by titrating the resulting potassic ferrocyanide with permanganate, 2 eq. of which $=1$ eq. of MnO^2.

The results are very satisfactory with certain precautions suggested by Fresenius, namely:—

1. That the solution of caustic potash or soda used must be free from organic matter; if pure solid alkalies are used, they should be fused in a silver crucible before being added.

2. That the boiling must not be continued too long, for if pure potash and ferricyanide are boiled for some considerable time, traces of ferrocyanide are produced.

3. The precipitate must be exceedingly well washed; and being rather voluminous, this occupies some time.

The Analytical process: The acid solution of manganous oxide is mixed with a solution of ferric chloride, in such proportion that not less than 1 eq. of Fe^2O^3 is present with every 1 eq. of MnO. The mixture is then added, little by little, to a boiling alkaline solution of potassic ferricyanide; after a few minutes boiling, the precipitate becomes granular, and shrinks somewhat. It is then put aside till *quite* cold (the hot solution would be affected by the reducing action of the filter), then filtered and thoroughly washed; the filtrate, or a portion of it, after acidifying with sulphuric acid and warming, is titrated with permanganate.

A shorter but somewhat less exact method is to dilute the mixture after boiling, to a definite volume, say 300 c.c.; allow to settle thoroughly; then take out 100 c.c. or so for titration. The bulky precipitate interferes, to a small extent, with the accurate measurement of the liquid; and this difficulty is increased when a great excess of ferric oxide is present. A mean of five determinations made by Fresenius on this plan, using only a slight excess of iron, gave 99·12 instead of 100; the process is therefore quite satisfactory for cases where the greatest accuracy is not required.

2. By Precipitation with Potassic Permanganate, (Guyard.)

If a dilute neutral or faintly acid solution of manganous salt be heated to 80°C. and permanganate added, hydrated MnO^2 is precipitated and the end of the reaction is known by the occurrence of the usual rose colour of permanganate in excess—the reaction is exact in neutral solutions, any large excess of either HCl or H^2SO^4 causes irregularity, as also do ferric or chromic salts; nickel, cobalt, zinc, alumina, or lime, in moderate quantity are of no consequence.

The Analytical process. 1 or 2 gm. of the manganese compound is dissolved in *aqua regia*, boiled a few minutes, the excess of acid neutralized with alkali, then diluted largely with boiling water, (1 or 2 litres) kept at a temperature of 80°C., and standard permanganate added so long as a brownish precipitate forms, and until the clear supernatant liquid shows a distinct rose colour; 2 eq. of permanganate=3 eq. of manganese, therefore, 1 c.c. of $\frac{N}{10}$ solution $= 0·0016542$ gm. of Mn.

3. By Precipitation as Oxalate, (Wolcott Gibbs.)

This method is similar to that given for zinc, § 45. 6, and owing to the fact that nickel, cobalt, and other metals of the same class are precipitated by the same agent, the use of the process is exceedingly limited, the treatment is the same as for zinc, the results are slightly too low but sufficiently exact for technical purposes.

4. By precipitation as Ammonia Phosphate, (Wolcott Gibbs.)

Manganese protosalts can be precipitated from solutions containing ammonia and ammonic chloride by sodic phosphate in the same way as magnesium salts, the precipitate is practically insoluble in hot water, either with or without ammonia and ammonic chloride. In order to separate the manganese compound in a dense and crystalline form, a considerable excess of sodic phosphate is required, the mixture must be well boiled and afterwards digested at a temperature near boiling. By using a standard solution of sodic phosphate in large quantity, whose exact strength when duly diluted and in the presence of ammonia salts is found by uranium, the proportion of phosphoric acid in combination with the manganese can be found.

The precipitate has the formula $P(MnNH^4)O^4 + H^2O$. 1 c.c. of normal sodic phosphate = 0·01838 gm. of Mn.

5. Colour Titration of Manganese in Pig Iron, Steel, and Iron Ores. (Bremner.)

0·1 gm. of a substance similar to the sample, and containing a known quantity of manganese, is placed in a crucible holding about 30 c.c., and 2 c.c. of concentrated nitric acid are added; the contents are then evaporated to dryness, and ignited till all red fumes disappear. The residue, crushed to a fine powder with a platinum spatula, is heated with 2 c.c. of concentrated potash solution, all spirting being avoided, and when again dry is gently ignited. The fused mass, after cooling, is treated with 25 c.c. of water, and well stirred. After settling for ten minutes. 5 c.c. of the clear green liquid are very carefully taken up with a pipette, and placed in a graduated test-tube. This solution being taken as the standard, the same weight of the sample to be tested is taken and treated in precisely the same manner, and under the same conditions. Should the green be of deeper tint in this than in the standard, water is added to the former till the tints coincide, the increased volume indicating proportionately more manganese present in the sample, equality of volume and tint indicating equal amounts of manganese present in each. If in any case difficulty be found in comparing the tints, on account of difference of shades of colour, a drop of sulphuric acid in each tube will produce the red permanganate, which yields a still more delicate comparison. In this case, however, manganese peroxide is quickly deposited, producing turbidity, and hence the last-named plan is resorted to only in cases of emergency. The accuracy of this method has been proved by comparison with that in which the manganese was estimated by direct weighing as sulphide, with very fair results, but considerable practice is required to insure accuracy.

6. Estimation of Manganese in small quantities, (Chatard.)

This method depends upon the production of permanganic acid by the action of nitric acid and lead peroxide, the accuracy of the process as a quantitative one can, however, only be depended on when the quantity of manganese is very small, such as exists in some minerals, soils, &c.

The material to be examined is dissolved in nitric acid and boiled with lead peroxide, by which means any manganese present is converted to permanganate, the quantity so produced is then ascertained by a weak freshly made standard solution of oxalic acid or ammonic oxalate.

The author found the process to give good results in determining manganese in dolomites and limestones, where the proportions amounted to from $\frac{1}{10}$ to 2 per cent., in larger quantities the total conversion of the manganese cannot be depended on.

Peters avails himself of this method for estimating manganese in pig iron or steel by weighing 0·1 gm. of the sample, and boiling in 3 or 4 c.c. of nitric acid until solution of the metal is complete, adding 0·2 or 0·3 gm. PbO^2, and again boiling for two or three minutes without filtering off the insoluble graphite if such should be present; the solution is then cooled, filtered through asbestos into a suitable graduated tube, and the colour compared with a standard solution of permanganate contained in a similar tube.

The standard permanganate is best made by diluting 1 c.c. of $\frac{N}{10}$ solution with 109 c.c. of water, each c.c. will then represent 0·00001 gm. Mn. It has been previously mentioned that accurate results by this method can only be obtained by using very small quantities of material. Peters finds this to be the case, and hence recommends, that for irons containing from 0·10 to 0·35 per cent. of Mn. 0·1 gm. should be operated upon, when from 0·8 to 1 per cent. is present, 0·1 gm. of the sample is weighed and one-fourth of the solution only treated with PbO^2; in still richer samples proportionate quantities must be taken. As a guide, it is well to assume, that when the amount of iron taken yields a colour equal to 25—35 c.c. of the standard, the whole of the Mn is oxidized—the actual amount of manganese in any test should not exceed half a milligramme. (Chem. News, vol. xxxiii, p. 35.)

7. Estimation in Spiegeleisen, Steel, &c., by measurement of CO^2. (Parry.)

Parry avails himself of the well known reaction in Fresenius and Wills' process of decomposing MnO^2 with sulphuric or hydrochloric acid and sodium oxalate, by dissolving a known weight of spiegeleisen in strong nitric acid, in a small pear-shaped flask o hard glass; evaporating to dryness, igniting gently for ten minutes and after cooling treating the residue with sodic oxalate an hydrochloric acid, connecting the flask immediately to the ga apparatus and conveying the evolved CO^2 into it for measuremen over mercury. **Parry** uses an apparatus devised by himself, an figured in his paper, (Chem. News, vol. xxix, p. 86); but the bes apparatus is decidedly **Frankland** and **Armstrong's**, shown i fig. 32, and such as is used by them in the analysis of wate residues, (Part 6); or the larger apparatus devised by **McLeod** and figured in Part 7, may be used. The number of c.c. of CO at 760°m.m. pressure and 0° C. temperature being known, it is eas to calculate the corresponding quantity of of manganese.

87 parts by weight of MnO^2=88 CO^2=55 Manganese.

It was, however, found impossible to obtain a product containin MnO^2. Although many experiments were made with this object heating over the **Bunsen's** burner as previously described, th manganese was always present as Mn^2O^3, and further heating fo thirty minutes showed no loss of oxygen. Consequently, 88 part of CO^2 represented 110 of metallic manganese.

Example.

0·5 gm. of Spiegeleisen gave CO^2	31·80 c.c.
Temperature	19·00°
Barometer	738·00 m.m.
Tension of aqueous vapour ...	16·36 „

$$\frac{31{\cdot}8 \times 721{\cdot}64}{760 \times \{1 + (0{\cdot}003665 \times 19)\}} =$$

$$= \frac{28{\cdot}22 \text{ c.c. } CO^2 \times 0{\cdot}1966 \times 110}{88} =$$

$$= 0{\cdot}06934 \text{ gm. Mn.}$$

Manganese ... ... 13·868 per cent.

The above calculations appear rather tedious, but they take les time than when manganese is estimated by precipitation, the latte process requiring at least six hours, and in most instances muc longer. The calculation may also be simplified by the use of th tables given at the end of this book, where the divisor for th formula—

$$\frac{V \times B}{760 \times (1 \times \delta t)}$$

is given. Also the value of 1 c.c. of CO^2 shown by the instrumen may be expressed in parts by weight of Mn. Thus, 28·22 c.c of CO^2=0·06934 gm. of CO^2; therefore, 1 c.c.=0·00245716 gm of Mn, which, multiplied by x c.c. of CO^2 found, gives at once th corresponding amount of manganese.

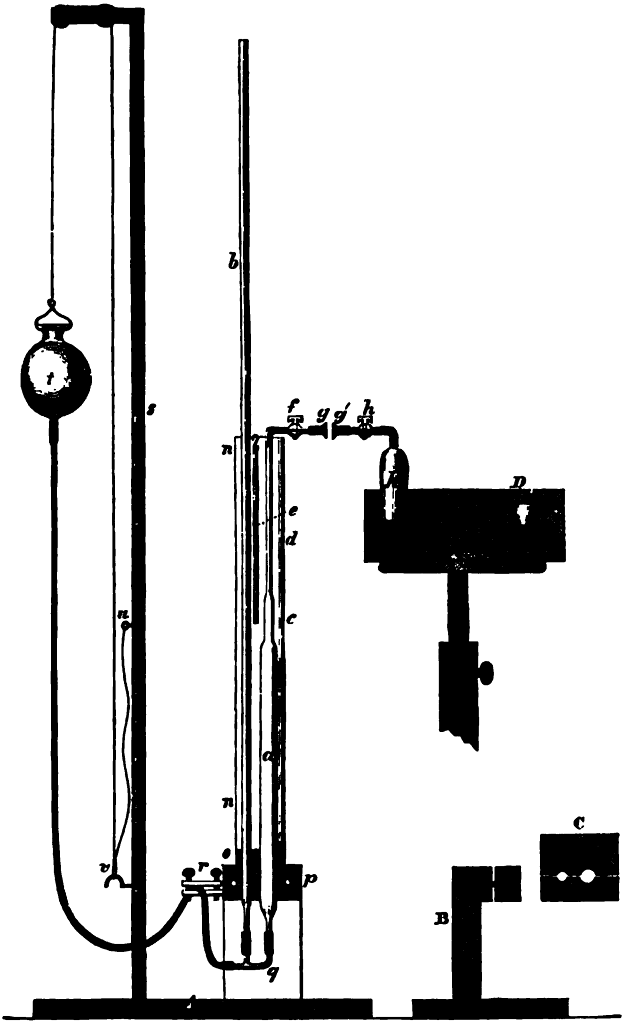

Fig. 32.

*** By an oversight the graduation of the tubes was omitted in this figure.

Examples.

0·500	gm. of	Spiegeleisen	gave	28·20	c.c. of CO^2	=13·860°/$_0$	of Mn
”	”	”		28·05	”	=13·800	”
By weight—Manganese				...	...	13·740°/$_0$	
0·500	gm. of	Spiegeleisen	(1) gave	23·57	of c.c. CO^2	=11·600°/$_0$	of Mn
”	”	”	(2)	”	”	”	”
”	”	”	(3)	”	”	”	”
”	”	”	(4)	”	”	”	”
”	”	”	(5)	”	”	”	”
0·253	”	”		11·70	”	11·500	”
0·264	”	”		12·60	”	11·350	”
0·250	”	”		11·80	”	11·590	”
1·000	”	”		47·00	”	11·547	”
By weight		...		...	...	11·530	”

This method has been applied to the determination of manganese in steel, treating not less than 4 gm. of steel, and measuring over mercury. The dry product requires a rather stronger heat, best obtained by heating over a small Bunsen's burner in an open platinum capsule. It is best to take 10 gm. of steel, evaporate to dryness in a porcelain dish, and heat a weighed portion of the dry residue as above, reserving part for a second trial.

8. Technical Examination of Manganese Ores, Pyrolusite, Braunite, Manganite, Psilomelane, &c.

One of the most important things connected with the analysis of Manganese ores is the determination of moisture; and as disputes arise sometimes between analysts and those who buy and sell, simply because the sample examined by one analyst contained more or less moisture than one from the same bulk examined by another, it is always best to mention the amount of moisture found in the sample upon the certificate of analysis. Fresenius has found by a most careful series of experiments that the temperature at which all hygroscopic moisture is expelled, without disturbing that which is chemically combined, is 120° C., and this temperature is now used by most English and continental chemists. The drying apparatus devised by Fresenius consists of a round cast-iron air chamber, about ten inches in diameter and two inches deep, having six openings at the top, into which little brass pans, two and a half inches diameter, are dropped, containing the very finely powdered ore; into one of the pans the bulb of a thermometer is placed, imbedded in iron filings, and the instrument kept upright by an iron rod and ring attached to the upper surface of the air chamber; the whole is supported by a tripod, and heated by a gas flame to the required temperature.

As only those who are continually analysing manganese ores would require a drying apparatus of this kind, a simpler contrivance is desirable for occasional use, and this is best managed by a common iron ladle: it can be supported upon a retort ring, and heated by a gas or spirit lamp, using a tube thermometer for stirring the powder, and keeping it at a temperature of about 115° C. for about an hour, and lastly raising it to 120°, keeping it constantly stirred; then remove the heat, empty the powder into a porcelain crucible or dish, and let it cool somewhat under the exsiccator; before it is quite cold transfer to a small stoppered and accurately weighed bottle. The ore, when powdered and dried at this temperature, rapidly absorbs moisture on exposing it to the air, and consequently if a definite quantity has to be weighed it must be done quickly; therefore it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which with its contents and stopper is accurately known; about 1 or 2 gm. or any other quantity within a trifle can be emptied into the proper vessel for analysis, and the exact quantity found by re-weighing the bottle after the stopper is inserted.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to insure its complete and rapid decomposition by the hydrochloric acid.

Considerable discussion has arisen of late as to the best processes for estimating the available oxygen in manganese ores, arising from the fact that many of the ores now occurring in the market contain iron in the ferrous state, and if such ores be analysed by the usual iron method with hydrochloric acid, a portion of the chlorine produced is employed in oxidising the iron contained in the original ore. Such ores, if examined by Fresenius and Wills' method, show therefore a higher percentage than by the iron method, since no such consumption of chlorine occurs in the former process. Manufacturers have therefore refused to accept certificates of analysis of such ores when based on Fresenius and Wills' method. This renders the volumetric processes of more importance, and hence various experiments have been made to ascertain their possible sources of error.

The results show that the three following methods give very satisfactory results. (See Scherer and Rumpf., "Chem. News," vol. xx. p. 302; also Pattinson, *ibid.*, vol. xxi. p. 266; and Paul, vol. xxi. p. 16.)

9. Direct Analysis by Distillation with Hydrochloric Acid, and Titrating with Sodic Hyposulphite.

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of Manganese or mixtures of them; it also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and, further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The apparatus necessary for the operation is shown in figs. 23, or 32. For precautions in conducting the distillation, see § 33.

In order that the percentage of peroxide shall be directly expressed by the number of c.c. of $\frac{N}{10}$ hyposulphite solution used, 0·436 gm. of the properly dried and powdered sample is weighed and put into the little flask; solution of potassic iodide in sufficient quantity to absorb all the iodine set free is put into the large tube (if the solution containing $\frac{2}{10}$ eq. or 33·2 gm. in the litre be used, about 70 or 80 c.c. will in ordinary cases be sufficient; hydrochloric acid is then poured into the distilling flask, and the operation conducted as in § 33.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample bottle into the flask, and find the exact weight afterwards.

10. Estimation by Oxalic Acid.

The very finely powdered ore is brought in contact with a known volume of normal oxalic acid solution, sulphuric acid added, and the mixture heated and well shaken to bring the materials in contact and liberate the carbonic acid; when the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume, say 300 c.c., and 100 c.c. of the dirty milky fluid, well acidified, diluted, and titrated for the excess of oxalic acid by permanganate; if, in consequence of the impurities of the ore, the mixture be brown or reddish coloured, this would of course interfere with the indication of the permanganate, and consequently the mixture in this case must be filtered; the 300 c.c. are therefore well shaken and poured upon a large filter; when about 100 c.c.

have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution be not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of its well-known bright rose-red; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4·357 gm. of the ore be weighed for analysis, the number of c.c. of normal oxalic acid will give the percentage of peroxide; but as hat is rather a large quantity, and takes some time to dissolve and ecompose, half the quantity may be taken, when the percentage obtained by doubling the volume of oxalic acid.

Example: The permanganate was titrated with normal oxalic acid d it was found that 1 c.c.=0·25 c.c. of normal oxalic acid. 178 gm. of a fine sample of commercial manganese (Pyrolusite) ere treated with 50 c.c. of normal oxalic together with 5 c.c. of ncentrated sulphuric acid until the decomposition was complete; e resulting solution was milky, but contained nothing to obscure e colour of the permanganate, and, therefore, needed no filtration; was diluted to 300 c.c. and 100 c.c. taken for titration, which quired 6·2 c.c. of permanganate; a second 100 c.c. required 6·3, ean 6·25, which multiplied by 3 gave 18·75 c.c.; this multiplied y the factor 0·25 to convert it into oxalic acid, gave 4·68 c.c. rmal oxalic, and this being deducted from the original 50 c.c. ed, left 45·32 c.c.=90·64% of pure manganic oxide.

This process possesses an advantage over the following inasmuch there is no fear of false results occurring from the presence of r; the analysis may be broken off at any stage, and resumed at e operator's convenience.

11. Estimation by Iron.

The most satisfactory form of iron to be used in this process is in annealed iron wire, which is extremely pure, and readily luble in sulphuric acid; if a perfectly dry and unoxidised double on salt be at hand, its use saves time; 1 molecule of this salt = 392, presenting 43·5 of manganic peroxide, consequently, 1 gm. of pure eroxide requires 9 gm. of the double salt; or in order that the perentage shall be obtained without calculation 1·111 gm. of ore may e weighed and digested in the presence of free sulphuric acid, with 0 gm. of double salt, the whole of which would be required supposing e sample were pure peroxide. The undecomposed iron salt remaining at the end of the reaction is estimated by potassic permanganate r bichromate; the quantity so found is deducted from the original 0 gm., and if the remainder be multiplied by 10 the percentage of xide is gained.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of double salt, the weight of which is known; after the undecomposed quantity is found by permanganate or bichromate, the remainder is multiplied by the factor 0·111, which gives the proportion of pure peroxide present, whence the percentage may be calculated.

The decomposition of the ore may very conveniently be made in the flask apparatus, fig. 29. The ore is first put into the decomposing flask, then the iron salt and water, so as to dissolve the salt to some extent before the sulphuric acid is added. Sulphuric acid should be used in considerable excess, and the flask heated by the spirit lamp till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate or bichromate. Instead of this apparatus, a single flask, with bent tube dipping under water, will be equally convenient.

Example: 1 gm. of double iron salt was titrated with permanganate solution, of which 21·4 c.c. were required.

A portion of the prepared ore was shaken out of the sample bottle, and found to weigh 1·24 gm.; ten grammes of double salt, with a little water, were added (where many manganese analyses are made, it is convenient to keep the required quantity weighed in small tubes well corked), and sulphuric acid poured in; after the decomposition was complete, 32·5 c.c. of permanganate were required to titrate the undecomposed iron salt; consequently

$$21·4 : 1 :: 32·5 : 1·51.$$

1·51 gm., therefore, being deducted from 10 gm., left 8·49 gm., which multiplied by 0·111, gave 0·942 gm. of pure peroxide, whence the percentage is as follows—

$$1·24 : 0·942 : 100 : x = 75·9\%$$

1·111 gm. of the same sample was accurately weighed and digested with 8 gm. of iron salt, and sulphuric acid as before; after the decomposition 8·8 c.c. of permanganate were required to peroxidise the undecomposed iron salt = 0·42 gm., which deducted from the 8 gm. originally used, left 7·58 gm.; or placing the decimal point one place to the right, 75·8% of pure manganic peroxide.

In the last example, 8 gm. of iron salt were used, because from the former experiment the percentage of peroxide was known, and therefore it was not necessary to exceed the required quantity to any great extent: as most samples do not contain more than 80 per cent., 8 gm. is sufficient.

In the case of using $\frac{N}{10}$ bichromate for the titration, the following plan is convenient: 100 c.c. of $\frac{N}{10}$ bichromate = 3·92 gm. of double iron salt: (supposing it to be perfectly pure,) therefore if 0·436 gm. of the sample of ore be boiled with 3·92 gm. of the double salt and excess of acid, the number of c.c. of bichromate required deducted from 100 will leave the number corresponding to the percentage.

Example: 0·436 gm. of the same sample as examined before, was boiled with 3·92 gm. of double salt, and afterward required 24 c.c. of $\frac{N}{10}$ bichromate, which deducted from 100, leaves $76^{\circ}/_{0}$ of oxide, agreeing very closely with the previous examinations.

When using metallic iron for the titration (which in most cases is desirable), Pattinson proceeds as follows:—30 grs. of clean iron wire are placed in the apparatus fig. 29, with 3 oz. of dilute sulphuric acid, made by adding 3 parts of water to 1 of concentrated acid. When the iron is quite dissolved, 30 grs. of the finely powdered and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 8 or 10 oz. with distilled water. The amount of iron remaining unoxidised in the solution is then ascertained by means of a standard solution of potassic bichromate. The amount indicated by the bichromate deducted from the total amount of iron used, gives the amount of iron which has been oxidised by the manganese ore, and from which the percentage of manganic peroxide contained in the ore can be calculated. Thus, supposing it were found that 4 grs. of iron remained unoxidised, then $30-4=26$ grs. of iron which have been oxidised by the 30 grs. of ore. Then, as

$$\begin{array}{ccccccc} \mathrm{Fe} & & \mathrm{MnO^2} & & \mathrm{Fe} & & \mathrm{MnO^2} \\ 56 & : & 43{\cdot}5 & :: & 26 & : & 20{\cdot}2 \end{array}$$

the amount of peroxide in the 30 grs. of ore. The percentage is, therefore, 67·33. Thus—

$$30 : 20{\cdot}2 :: 100 : 67{\cdot}33.$$

Grain weights are given in this example, but those who use the gramme system will have no difficulty in arranging the details accordingly.

DETERMINATION OF THE AMOUNT OF HYDROCHLORIC ACID REQUIRED TO DECOMPOSE MANGANESE ORES.

Although two samples of ore may contain the same amount of available peroxide, they may, from the presence of carbonates, or from different chemical constitution, require varying amounts of hydrochloric acid to liberate chlorine, and insure the complete decomposition of the ore. In order to ascertain the effect of such ores upon hydrochloric acid, it is only necessary to take 10 or 20 c.c. of acid of known gravity, dilute with water, and find the actual amount of acid by Kieffer's solution § 23. 1 gm. or thereabout of the ore is then heated with a measured quantity of the same acid in sufficient excess to insure complete decomposition, —best done in a small flask with a long tube through the cork, bent slightly, so that any acid which may be volatilized shall return to the flask—the chlorine expelled completely by heat, then the gangue filtered away, washed, and the filtrate diluted to a given measure, and a known volume taken for titration of free acid present. 1 gm. of ore and 10 to 12 c.c. acid of sp. gr. 1·1 are convenient quantities to use.

NICKEL.

Ni = 59.

§ 47. This metal when existing in solution in a tolerably pure state can be estimated according to Künzel by precipitation with sodic sulphide, using as indicator either sodic nitroprusside or ammoniacal silver solution; or by distillation with hydrochloric acid into potassic iodide, the liberated iodine being titrated with hyposulphite; or again, it can be precipitated as monoxide, and estimated alkalimetrically with normal nitric acid. Further, it can be estimated as oxalate in the same way as zinc § 45.6.

The application of any of these processes is, however, exceedingly limited.

COBALT.

Co = 59.

1. Estimation by Mercuric Oxide and Permanganate (Winkler).

§ 48. If an aqueous solution of cobaltous chloride or sulphate be treated with moist finely divided mercuric oxide no decomposition ensues, but on the addition of permanganate to the mixture, hydrated cobaltic and manganic oxides are precipitated. It is probable that no definite formula can be given for the reaction, and therefore practically the working effect of the permanganate is best established by a standard solution of cobalt of known strength, say metallic cobalt dissolved as chloride, or neutral cobaltous sulphate.

The Analytical process: The solution, free from any great excess of acid, is placed in a flask, diluted to about 200 c.c., and a tolerable quantity of moist mercuric oxide (precipitated from the nitrate or perchloride by alkali and washed) added. Permanganate from a burette is then slowly added to the cold solution with constant shaking until the rose colour appears in the clear liquid above the bulky brownish precipitate.

The appearance of the mixture is somewhat puzzling at the beginning, but as more permanganate is added the precipitate settles more freely, and the end as it approaches is very easily distinguished; the final ending is when the rose colour is persistent for a minute or two; subsequent bleaching must not be regarded.

The actual decomposition as between cobaltous sulphate and permanganate may be formulated thus—

$$6CoSO^4 + 5H^2O + 2MnKO^4 = K^2SO^4 + 5H^2SO^4 + 3Co^2O^3 + 2MnO^2$$

but as this exact decomposition cannot be depended upon in all the mixtures occurring, it is not possible to accept systematic numbers calculated from normal solutions.

Solutions containing manganese, phosphorus, arsenic, active chlorine or oxygen compounds, or organic matter, cannot be used in this estimation; moderate quantities of nickel are of no consequence.

CALCIUM.

Ca = 40.

1 c.c. $\frac{N}{10}$ permanganate = 0·0028 gm. CaO
" " = 0·0050 gm. $CaCO^3$
" " = 0·0086 gm. $CaSO^4 + 2H^2O$
" normal oxalic acid = 0·0280 gm. CaO
Cryst. oxalic acid × 0·444 = CaO
Double iron salt × 0·07143 = CaO

§ 49. The estimation of lime alkalimetrically has already been given, § 20 but that method is of limited application, unless calcic oxalate, in which form lime is generally separated from other bases, be converted into carbonate or caustic lime by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel, are as exact in their results as the determination of lime by weight; and where a series of estimations have to be made the plan is very convenient.

The Analytical process: 1. The lime is precipitated by ammonic oxalate from an ammoniacal or acetic acid solution, the precipitate well washed, then together with the filter, pushed through the funnel into a large flask, acidified, and diluted freely: then titrated with permanganate, as described in § 28.4.

$$63\ \bar{O} = 28\ \mathrm{CaO}$$

2. This process is applicable in certain cases only, but saves time when it can be applied. To the lime solution (which must contain no substance capable of decomposing permanganate) a measured excess of normal oxalic acid is added; the precipitated calcic oxalate allowed to settle in a 300 c.c. flask, and 100 c.c. of the clear liquid acidified and titrated for the excess of oxalic acid; the quantity so found is multiplied by 3, deducted from that originally added, and the remainder multiplied by the factor for normal oxalic acid.

BISMUTH.

Bi = 210.

§ 50. Buisson and Ferray (Moniteur Scientifique, 3 ser., iii, 900) have announced a method of estimating bismuth by means of iodic acid, which is said to give very satisfactory results in the case of commercial bismuth compounds, more especially the basic nitrate commonly used in pharmacy.

The method is based upon the complete precipitation of bismuth by iodic acid and acetic acid solution, and in the case of bismuthic nitrate is conducted as follows:

0·5 gm. of the salt to be examined is dissolved by the aid of nitric acid in a small quantity of water, then sodic bicarbonate added until a small but persistent precipitate is produced: this precipitate is redissolved by an excess of acetic acid, (which prevents further precipitation on diluting with water,) the fluid is then heated to boiling, and insoluble compounds of iron and bismuth oxychloride filtered off; the filtrate and washings are mixed, and 25 c.c. of iodic solution added, (made by dissolving about 30 gm. of crystallised iodic acid in a litre of water,) then diluted to 250 c.c. After the mixture has stood a short time, it is filtered through a dry filter, and 100 c.c. titrated by adding to it dilute sulphuric acid and excess of potassic iodide; the amount of uncombined iodic acid is thus decomposed and the iodine which is set free, estimated by $\frac{N}{10}$ hyposulphite, and so the quantity of iodic acid combined with bismuth as bismuthic iodate is found.

The disappearance of the yellow colour is taken as the end of the process, and this being very easily recognized, there is no need for the use of starch liquor as indicator.

The actual power of the iodic acid in relation to the hyposulphite solution is first found by taking a measured portion, adding sulphuric acid and potassic iodide in sufficient excess to dissolve the liberated flakes of iodine, then delivering into the mixture the hyposulphite from a finely graduated burette until the yellow colour just disappears.

A measured quantity of a standard solution of pure metallic bismuth in nitric acid is then taken, treated with sodic bicarbonate, acidified with acetic acid, and the titration with measured quantities of iodic acid solution and hyposulphite conducted as previously described.

All the reagents must be free from chlorine, and of course the potassic iodide must be free from iodate.

CADMIUM.

$Cd=112$.

§ 51. This metal can be estimated by precipitation as sulphide, digesting in a stoppered flask with ferric chloride and hydrochloric acid, till decomposed, and the resulting ferrous compound, titrated with permanganate; each c.c. $\frac{N}{10}$ solution so required=0·0056 gm. of Cd or 0·0064 gm. of CdO; or the metal may be precipitated as carbonate, and estimated alkalimetrically with normal nitric acid, and Kieffer's solution. And again the estimation may be made with good results, when the metal exists as sulphate or nitrate, by oxalic acid, as in the case of Zinc, § 45,6; the process is precisely the same as there described.

TIN.

$Sn=118$.

Metallic iron × 1·0536 = Tin.
Double iron salt × 0·1505 = „
Factor for $\frac{N}{10}$ iodine or permanganate solution 0·0059

§ 52. The method, originally devised by Streng for the direct estimation of tin by potassic bichromate, or other oxidising agents in acid solution, has been found most unsatisfactory, from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride, there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, and which are found satisfactory.

Direct Titration by Iodine in Alkaline Solution (Lenssen).

Metallic tin or its protosalt if not already in solution, is dissolved in hydrochloric acid, and a tolerable quantity of the double tartrate of soda and potash added, together with sodic bicarbonate in excess. If enough tartrate be present, the solution will be clear; starch liquor is then added, and the mixture titrated with $\frac{N}{10}$ iodine, till the blue colour is permanent; metallic tin is best dissolved in hydrochloric acid by placing a platinum crucible or cover in contact with it so as to form a galvanic circuit. See also § 41.7.

2. Indirect Titration by Ferric Chloride and Permanganate, (Lowenthal, Stromeyer, &c).

This method owes its value to the fact that when stannous chloride is brought into contact with ferric or cupric chloride, it acts as a reducing agent, in the most exact manner, upon these compounds, stannic chloride being formed, together with a proportionate quantity of ferrous or cuprous salt, as the case may be; if either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron,—

$$SnCl^2 + Fe^2Cl^6 = SnCl^4 + 2FeCl^2.$$

56 iron=59 tin. If decinormal permanganate, or the factor necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

The solution of stannous chloride, or other protosalt of tin in hydrochloric acid, or the granulated metal, is mixed with pure ferric chloride, which if tolerably concentrated, dissolves metallic tin readily, and without evolution of hydrogen, then diluted with distilled water, and titrated with permanganate as usual; to obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which ferric chloride is added; the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Stannic salts, also tin compounds containing iron, are dissolved in water, hydrochloric acid added, and a plate of clean zinc introduced for ten or twelve hours; the tin so precipitated is carefully collected and washed, then dissolved in hydrochloric acid, and titrated as above; or the finely divided metal may at once be mixed with an excess of ferric chloride, a little hydrochloric acid added, and when solution is complete, titrated with permanganate; 4 eq. of iron (=224) occurring in the form of ferrous chloride, represent 1 eq. (=118) of tin.

Tin may also be precipitated from slightly acid peroxide solution as sulphide, by sulphuretted hydrogen gas or water, the sulphide well washed, and mixed with ferric chloride; the mixture gently warmed, the sulphur filtered off, and the filtrate then titrated with permanganate as above: 4 eq. of iron = 1 eq. of tin.

URANIUM.

Ur. = 118·8.

§ 53. THE estimation of uranium may be conducted with great accuracy by permanganate, in precisely the same way as ferrous salts, § 28. The metal must be in solution either as acetate, sulphate, or chloride, but not nitrate. In the latter case it is necessary to evaporate to dryness with excess of sulphuric or hydrochloric acid, or to precipitate with alkali, wash and redissolve in acetic acid.

The reduction to the uranous state is made with zinc, but as the end of reduction cannot, like iron, be known by the colour, it is necessary to continue the action for a certain time; in the case of small quantities a quarter, larger half an hour, at a temperature of 50° to 60°C., and in the presence of excess of sulphuric acid; hydrochloric acid may be used, but in that case the precautions mentioned on page 65 must be observed as with iron: all the zinc must be dissolved before titration. The solution is then freely diluted with boiled water, sulphuric acid added, if necessary, and then permanganate until the rose colour is faintly permanent: the ending is very distinct if the solution be well diluted, and the reaction is precisely the same as in the case of ferrous salts, namely, 2 eq. of uranium existing in the uranous state require 1 eq. of oxygen to convert them to the uranic state, hence 56 Fe = 118·8 Ur., consequently the strength of any permanganate solution in relation to iron being known, it is easy to find the amount of uranium. By using $\frac{N}{10}$ solutions systematic numbers are of course obtained and no calculation is required.

LEAD.

Pb. = 207.

1 c.c. $\frac{N}{10}$ permanganate = 0·01035 gm. Lead.
1 c.c. normal oxalic acid = 0·1035 gm. „
Metallic iron × 1·848 = „
Double iron salt × 0·264 = „
Crystallised oxalic acid × 1·643 = „

§ 54. The estimation of lead is in most cases more securely effected by weight than by measure; there are, however, instances in which the latter process may be used with advantage, and consequently the following methods are given:—

1. As Oxalate (Hempel).

The acetic lead solution, which must contain no other body precipitable by oxalic acid, is put into a 300 c.c. or dm. flask, and a measured quantity of normal oxalic acid added in excess, ammonia is then added to slight predominance, the flask filled to the mark with water, shaken, and put aside to settle; 100 c.c. of the clear liquid may then be taken, acidified with sulphuric acid, and titrated with permanganate for the excess of oxalic acid; the amount so found multiplied by 3, and deducted from that originally added, will give the quantity combined with the lead.

Where the nature of the filtrate is such that permanganate cannot be used for titration, the precipitate must be collected, well washed, dissolved in dilute nitric acid, with a considerable quantity of sodic acetate, sulphuric acid added, and titrated with permanganate.

In neither case are the results absolutely accurate, owing to the slight solubility of the precipitate, but with careful manipulation the error need not exceed 1 per cent.

2. As Chromate (Schwarz).

The lead is precipitated as chromate, well washed and digested with a weighed excess of double iron salt and hydrochloric acid; the resulting solution contains ferric and chromic chlorides, together with lead chloride, and undecomposed iron salt. The quantity of the last is found by permanganate, and deducted from the original weight; the remainder, multiplied by the factor 0·264, will give the weight of lead.

Schwarz has simplified this method as follows:—The standard solution being 14·73 gm. of pure potassic bichromate in a litre of water: 1 c.c. of this solution precipitates 0·0207 gm. of lead.

In the analysis of metallic lead, a certain quantity of it should e dissolved in a minimum of nitric acid, the solution diluted with rater, carefully neutralised with ammonia or sodic carbonate, xcess of sodic acetate added, and the solution precipitated by the ichromate solution. When the precipitation approaches its end, when the precipitate commences to subside readily, some drops a neutral solution of nitrate of silver are deposited on a porcelain ate, and the bichromate solution only added by two or three drops a time to the liquid under examination; after each addition the hole is well stirred, allowed to subside, and a drop of the clear liquor lded to one of the drops of the silver solution. As soon as the chromate is in excess the two drops form a red colour, while the ecipitated chromate of lead has no effect on the silver test, but mply floats on the top as a yellow precipitate. Should the solu- on assume a yellow colour before the silver reaction has commenced, would indicate that not sufficient acetate of soda had been added the first instance, and it would be necessary to add this now, and so a cubic centimetre of a normal lead solution, containing 0·0207 lead as nitrate. The slight turbidity which first takes place soon es off, and the operation may be proceeded with as before. One ibic centimetre must naturally, in such instance, be deducted from e amount of chrome solution, on account of the extra addition lead. Experiments made with 0·6975 gramme of the purest ad of Tarnowitz gave the following results:—It required 33·7 c. of bichromate solution, and as it is always necessary to have slight excess of bichromate, we may assume that 33·6 cubic ntimetres only were requisite for the precipitation of the lead. 3·6 multiplied by 0·0207 = 0·6955 gm. or = 99·72 per cent., howing that it was nearly pure lead.

0·399 gm. of well-dried lead nitrate required also 12 c.c. of ichromate indicating 0·2484 gm. of lead, or 62·29 per cent. ccording to calculation, lead nitrate should contain 62·54 per cent.

0·385 gm. of crystallised lead acetate required 10·2 c.c. of ichromate=0·211 gm., or 54·84 per cent. of lead, while accord- ng to the formula $Pb\bar{A}^2 + H^2O$, it should have been 54·61 per cent.

Neutral potassic chromate may be used instead of bichromate if esired.

Copper, cadmium, zinc, ferric salts, and cobalt, do not interfere rith the reaction—but all metals precipitable by chromic acid should f course be removed.

3. Alkalimetric Method (Mohr).

The lead is precipitated as carbonate by means of a slight excess of ammonic carbonate, together with free ammonia, the precipitate well washed, and dissolved in a measured excess of normal nitric acid; neutral solution of sodic sulphate is then added to precipitate the lead as sulphate; without filtering, the excess of nitric acid is then estimated by normal alkali, each c.c. combined being equal to 0·1035 gm. of lead.

4. Assay of Refined Metallic Lead.

Fresenius has published an extensive memoir (Zeitschrift, vol. viii. p. 148) on the estimation of the small quantities of other metals occurring in refined lead, and which have undoubtedly a considerable effect upon its value for many purposes, such as chambers for sulphuric acid manufacture, &c. The refining process is now generally carried on so well that refined soft lead can commonly be obtained containing from 99·94 to even 99·995% of pure lead. The metals usually found as impurities are silver, copper, antimony, bismuth, cadmium, zinc, iron, and nickel, with traces of cobalt, manganese, and arsenic. Of these the most commonly found are silver, iron, antimony, copper, and zinc, all of which, according to Fresenius' experiments, may be estimated volumetrically with greater exactness than by weight. The process of separation is fully described in the memoir alluded to, but as it is too lengthy for insertion here, those who desire to carry out the process are referred to the original article.

MERCURY.

$Hg = 200.$

1 c.c. $\frac{N}{10}$ solution = 0·0200 gm. Hg
= 0·0208 „ Hg^2O
= 0·0271 „ $HgCl^2$
Double iron salt × 0·5104 = Hg
„ „ × 0·6914 = $HgCl^2$

1. Precipitation as Mercurous Chloride.

§ 55. The solution to be titrated must not be warmed, and contain the metal only in the form of protosalt. $\frac{N}{10}$ sodic chloride is added in slight excess, the precipitate washed with the least possible quantity of water to ensure the removal of all the sodic chloride; to the filtrate a few drops of chromate solution are added, then pure sodic carbonate till the liquid is of clear yellow colour,

$\frac{N}{10}$ silver is then delivered in till the red colour occurs. The quantity of sodic chloride so found is deducted from that originally used, and the difference calculated in the usual way.

2. By Ferrous Oxide and Permanganate, (Mohr).

This process is based on the fact that when mercuric chloride (corrosive sublimate) is brought in contact with an alkaline solution of ferrous oxide in excess, the latter is converted into ferric oxide while the mercury is reduced to mercurous chloride (calomel), the xcess of ferrous oxide is then found by permanganate or bichromate—

$$2HgCl^2 + 2FeCl^2 = Hg^2Cl^2 + Fe^2Cl^6.$$

It is therefore advisable in all cases to convert the mercury to be stimated into the form of sublimate, by evaporating it to dryness rith nitro-hydrochloric acid; this must take place, however, elow boiling heat; as vapours of chloride escape with steam t 100° C. (Fresenius).

Nitric acid or free chlorine must be altogether absent during the ecomposition with the iron protosalt, otherwise the residual titraion will be inexact, and the quantity of the iron salt must be ore than sufficient to absorb half the chlorine in the sublimate.

Example: 1 gm. of pure sublimate was dissolved in warm water, nd 3 gm. of double iron salt added, then solution of caustic soda ill freely alkaline. The mixture became muddy and dark in colour, nd was well shaken for a few minutes, then sodic chloride and ulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of ferric oxide dissolved, leaving the alomel white; it was then diluted to 300 c.c., filtered through a ry filter, and 100 c.c. titrated with $\frac{N}{10}$ permanganate, of which 3·2 c.c. were required—13·2 × 3 = 39·6, which deducted from 6·5 c.c. (the quantity required for 3 gm. double iron salt,) left 6·9 c.c. = 1·446 gm. of undecomposed iron salt, which multiplied y the factor 0·6914, gave 0·999 gm. of sublimate, instead of 1 gm., r the 36·9 c.c. may be multiplied by the $\frac{N}{10}$ factor for mercuric hloride, which will give the same figures exactly.

3. By Iodine and Hyposulphite, (Hempel).

If the mercury exist as a protosalt it is precipitated by sodic hloride, the precipitate well washed, and together with its filter ushed through the funnel into a stoppered flask, a sufficient quantity of potassic iodide added, together with $\frac{N}{10}$ iodine solution (1 gm. of calomel about 2·5 gm. of iodide, and 100 c.c. of $\frac{N}{10}$ iodine the flask closed, and shaken till the precipitate has dissolved—

$$Hg^2Cl^2 + 6KI + 2I = 2HgK^2I^4 + 2KCl.$$

The brown solution is then titrated with $\frac{N}{10}$ hyposulphite ti colourless, diluted to a definite volume, and a measured portio titrated with $\frac{N}{10}$ iodine and starch for the excess of hyposulphit 1 c.c. $\frac{N}{10}$ iodine = 0·02 gm. Hg.

Where the mercurial solution contains nitric acid, or the meta exists as peroxide, it may be converted into protochloride by th reducing action of ferrous sulphate, as in Mohr's method. Th solution must contain hydrochloric acid or common salt in sufficien quantity to transform all the mercury into calomel. At least thre times the weight of mercury present of ferrous sulphate in solutio is to be added, then caustic soda in excess, the muddy liquid wel shaken for a few minutes, then dilute sulphuric acid added i excess, and the mixture stirred till the dark coloured precipitat has become perfectly white. The calomel so obtained is collecte on a filter, well washed, and titrated with $\frac{N}{10}$ iodine and hypo sulphite as above.

4. Direct Titration with Sodic Hyposulphite. (Scherer.)

The solution of hyposulphite is in all cases made by dissolvin $\frac{1}{20}$ eq. = 12·4 gm. of the salt in 1 litre of water, or by mixin equal volumes of $\frac{N}{10}$ hyposulphite and distilled water.

The reaction which takes place with hyposulphite in the case o mercurous nitrate is

$$Hg^2(NO^3)^2 + Na^2S^2O^3 = Hg^2S + Na^2SO^4 + N^2O^5.$$

With mercuric nitrate—

$$3Hg(NO^3)^2 + 2Na^2S^2O^3 = 2HgS.Hg(NO^3)^2 + 2Na^2SO^4 + 2N^2O^5.$$

With mercuric chloride—

$$3HgCl^2 + 2Na^2S^2O^3 + 2H^2O = 2HgS.HgCl^2 + 2Na^2SO^4 + 4HCl.$$

(*a.*) **Mercurous Salts.** The solution containing the metal only as a protosalt is diluted, gently heated, and the hyposulphite delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown colour. The sulphide settles freely, and allows the end of the reaction to be easily seen. 1 c.c. of hyposulphite solution is equal to 0·020 gm. Hg., or 0·0208 gm. Hg^2O.

(*b.*) **Mercuric Nitrate.** The solution is considerably diluted, put into a stoppered flask, nitric acid added, and the hyposulphite cautiously delivered from the burette, vigorously shaking meanwhile until the last drop produces no further yellow precipitate. Scherer recommends that when the greater part of the metal is precipitated, the mixture should be diluted to a definite volume, the precipitate allowed to settle, and a measured quantity of the clear liquid taken for the completion of the process; the analysis may then be checked by a second titration of the clear liquid, if needful. 1 c.c. hyposulphite is equal to 0·015 gm. Hg., or 0·0162 gm. HgO.

(*c.*) **Mercuric Chloride.** With mercuric chloride (sublimate) the end of the process is not so easily seen; the course of procedure is as follows:—The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the hyposulphite cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty looking colour. Filtration is necessary to distinguish the exact ending of the reaction, for which purpose Dr. Beale's filter, fig. 25, is useful.

Liebig's method is the reverse of that used for determining chlorides in urine, sodic phosphate being used as indicator in the estimation of mercury, instead of the urea occurring naturally in urine. The method is capable of very slight application. For details, see Analysis of Urine.

5. As Mercuric Iodide (Personne, Compt. Rend. lvi, 63).

This process is founded on the fact that if a solution of mercuric chloride be added to one of potassic iodide, in the proportion of 1 equivalent of the former to 4 of the latter, red mercuric iodide is formed, which dissolves to a colourless solution until the balance is overstepped, when the brilliant red colour of the iodide appears as a precipitate, which, even in the smallest quantity, communicates its tint to the liquid. The mercuric solution must always be added to the potassic iodide; a reversal of the process, though giving eventually the same quantitative reaction, is nevertheless much less speedy and dependable. The mercurial compounds to be estimated by this process must invariably be brought into the form of neutral mercuric chloride.

The standard solutions required are decinormal, made as follows:—

Solution of Potassic Iodide: 33·2 gm. pure salt is dissolved, and diluted to 1 litre—1 c.c.=0·01 gm. Hg., or 0·01355 gm. $HgCl^2$.

Solution of Mercuric Chloride: 13·55 gm. of the salt, with about 30 gm. pure sodic chloride (to assist the solution of the mercuric salt), are dissolved and diluted to 1 litre, 1 c.c.=0·1 gm. Hg.

The conversion of various forms of mercury into mercuric chloride is, according to Personne, best effected by heating with caustic soda or potash, and passing chlorine gas into the mixture, which is afterwards boiled to expel excess of chlorine (the mercuric chloride is not volatile at boiling temperature when associated with alkaline chloride); the solution is then cooled and diluted to a given volume, placed in a burette, and delivered into a measured volume of the decinormal potassic iodide until the characteristic colour occurs; it is preferable to dilute the mercuric solution considerably, and make up to a given measure, say 300 or 500 c.c.—and as a preliminary trial take 20 c.c. or so of potassic iodide solution, and titrate it with the mercuric solution approximately with a graduated pipette, the exact strength may then be found by using a burette of sufficient size.

ARSENIC.

$As = 75. \ As^2O^3 = 198.$

1. Oxidation by Iodine (Mohr).

§ 56. THE principle upon which the determination of arsenious acid by iodine is based is explained in § 34.

Experience has shown, that in the estimation of arsenious compounds by the method there described, it is necessary to use sodic bicarbonate for rendering the solution alkaline in preference to the neutral carbonate, as there is less chance of the iodine being affected by the bicarbonate than by the neutral salt.

To a neutral or watery solution, therefore, it is best to add about 20 or 25 c.c. of saturated solution of pure bicarbonate to every 0·1 gm. or so of As^2O^3, and then titrate with $\frac{N}{10}$ iodine and starch. When the solution is acid, the excess may be removed by neutral sodic carbonate, then the necessary quantity of bicarbonate added, and the titration completed as before.

1 c.c. $\frac{N}{10}$ iodine = 0·00495 gm. As^2O^3.

2. Oxidation by Potassic Bichromate, (Kessler.)

This method is exactly the same as is fully described in § 58 for antimony.

The arsenious compound is mixed with $\frac{N}{10}$ bichromate in excess in presence of hydrochloric acid and water, in such proportion that at least $\frac{1}{8}$th of the total volume consists of hydrochloric acid, sp. gr. 1·12.

The excess of bichromate is found by a standard solution of pure iron or of double iron salt with potassic ferricyanide as indicator; the quantity of bichromate reduced is, of course, the measure of the quantity of arsenious converted into arsenic acid.

$$1 \text{ c.c. } \frac{N}{10} \text{ bichromate} = 0{\cdot}00495 \text{ gm. } As^2O^3.$$

In cases where the direct titration of the hydrochloric acid solution cannot be accomplished, the arsenious acid is precipitated with H^2S (with arsenates at 70°C) the precipitate well washed, the filter and the precipitate placed in a stoppered flask together with Sat a ~~standard~~ solution of mercuric chloride in hydrochloric acid of 1·12 sp. gr., and digested at a gentle heat until the precipitate is white, then water added in such proportion that not less than $\frac{1}{7}$th of the volume of liquid consists of concentrated hydrochloric acid, $\frac{N}{10}$ bichromate is then added and the titration with standard ferrous solution completed as usual.

3. Indirect Estimation by Distilling with Chromic and Hydrochloric Acids (Bunsen).

The principle of this very exact method depends upon the fact, that when potassic bichromate is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 1 eq. chromic acid. See § 57. 2

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

$$As^2O^3 + 4Cl + 2H^2O = As^2O^5 + 4HCl.$$

Therefore every 4 eq. of chlorine, short of the quantity yielded when bichromate and hydrochloric acid are distilled alone, represent 1 eq. arsenious acid. The operation is conducted in the apparatus figs. 23, or 32, and the titration as in § 32.

4. By Precipitation as Uranic Arsenate (Bödeker).

The arsenic must exist in the state of arsenic acid (As^2O^5), and the process is in all respects the same as for the estimation of phosphoric acid, devised by Neubauer, Pincus, and myself, § 69. The strength of the uranium solution may be ascertained and fixed by pure sodic or potassic arsenate, or by means of a weighed quantity of pure arsenious acid converted into arsenic acid by boiling with strong nitric acid. The method of testing is precisely the same as with phosphoric acid, that is to say, the solution of uranium used for P^2O^5 will suffice, and if its exact strength as regards that body be known, a slight calculation will show the quantity to be used for arsenic acid; but it is, nevertheless, preferable to titrate it upon a weighed amount of arsenical compound, bearing in mind here, as in the case of P^2O^5, that the titration must take place under precisely similar conditions as to quantity of liquid, the amount of sodic acetate and acetic acid added, and the depth of colour obtained by contact of the fluid under titration with the yellow prussiate solution. See § 69.

The precipitate of uranic arsenate possesses the composition—

$$2Ur^2O^3,As^2O^5.=566.$$

5. As Trihydride with Silver Nitrate.

Houzeau, (Compt. rend. lxxv, 1823), makes use of the reaction between arsenic or antimony (existing in combination with hydrogen) and silver nitrate, and applies it especially to the estimation of small quantities of these metals in cases of poisoning, &c.

The gas generated in Marsh's apparatus and consisting of arsenic, or antimony, or both, in combination with hydrogen is passed into a weak standard solution of silver nitrate, and when the precipitation is complete the excess of silver is found by standard sodic chloride.

$$Ag.=0{\cdot}11574 \text{ As. or } 0{\cdot}1867 \text{ Sb.}$$

of course it is necessary to insure the conversion of all the metals into the form of trihydride and to eliminate the whole of the gas from the apparatus, a matter of some difficulty.

The arsenious acid may be estimated directly by precipitating the silver with excess of HCl, and titrating the filtered liquor with standard permanganate.

CHROMIUM.

Cr=52·5.

Factors.

Metallic iron	×	0·3123	=	Chromium
,,	×	0·5981	=	Chromic acid
,,	×	0·8784	=	Potassic bichromate
,,	×	1·926	=	Lead chromate
Double iron salt	×	0·0446	=	Chromium
,,	×	0·0854	=	Chromic acid
,,	×	0·1255	=	Potassic bichromate
,,	×	0·275	=	Lead chromate

1 c.c. $\frac{N}{10}$ solution = 0·003349 gm. CrO^3

,, ,, = 0·00492 gm. $K^2Cr^2O^7$

1. Reduction by Iron.

§ 57. The estimation of chromates is very simply and successfully performed by the aid of ferrous oxide, being the converse of the process devised by Penny for the estimation of iron. See § 31.

The best plan of procedure is as follows. A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular double sulphate of iron and ammonia; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid and small quantities of the iron salt, added from time to time with a dry spoon, taking care that none is spilled, until the mixture becomes green, and the iron is in excess, best known by a small drop being brought in contact with a drop of red prussiate of potash on a white plate; if a blue colour appears at the point of contact, the iron is in excess. It is necessary to estimate this excess, which is most conveniently done by $\frac{N}{10}$ bichromate being added until the blue colour produced by contact with the red prussiate gives place to a yellow brown. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the $\frac{N}{10}$ bichromate deducted from it, and the remainder multiplied by the factor required by the substance sought.

Example: 0·5 gm. pure potassic bichromate was taken for analysis, and to its acid solution 4·15 gm. double iron salt added. 3·3 c.c. of $\frac{N}{10}$ bichromate were required to oxidise the excess of iron salt; it was found that 0·7 gm. of the salt = 17·85 c.c. bichromate solution consequently 3·3 c.c. of the latter were equal to 0·12985 gm. iron salt; this deducted from the quantity originally used left 4·02015 gm., which multiplied by the factor 0·1255 gave 0·504 gm. instead of 0·5 gm.

In the case of lead chromate being estimated in this way, it is best to mix both the chromate and the iron salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before. Where pure double iron salt is not at hand, a solution of iron wire in sulphuric acid, freshly made and of ascertained strength, can of course be used.

2. Estimation of Chromates by Distillation with Hydrochloric Acid (Bunsen, results very accurate).

When chromates are boiled with an excess of hydrochloric acid in Fresenius', Bunsen's, or Mohr's distilling apparatus, figs. 23, or 32, every 1 eq. of chromic acid liberates 3 eq. chlorine. For instance, with potassic bichromate the reaction may be expressed as follows—

$$K^2Cr^2O^7+14HCl=2KCl+Cr^2Cl^6+7H^2O+6Cl;$$

if the liberated chlorine is conducted into a solution of potassic iodide, 3 eq. of iodine are set free, and can be estimated by $\frac{N}{10}$ hyposulphite, as in § 31. 3 eq. of iodine so obtained=381, represent 1 eq. chromic acid = 100·50. The same decomposition takes place by mere digestion, as described in § 33.

ANTIMONY.

Sb = 122.

1. Conversion of Antimonious Acid in Alkaline Solution into Antimonic Acid by Iodine (Mohr).

§ 58. ANTIMONIOUS oxide, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralised by sodic carbonate, then a cold saturated solution of sodic bicarbonate, added in the proportion of 20 c.c. to about 0·1 gm. Sb^2O^3; to the clear solution starch liquor and $\frac{N}{10}$ iodine are added until the blue colour appears; the colour disappears after a little time, therefore the first appearance of a permanent blue is accepted as the true measure of iodine required.

1 c.c. $\frac{N}{10}$ iodine = 0·0061 gm. Sb.

2. Oxidation by Potassic Bichromate or Permanganate, (Kessler.)

Bichromate or permanganate added to a solution of antimonious chloride, containing not less than $\frac{1}{8}$ of its volume of hydrochloric acid, sp. gr. 1·12, converts it into antimonic chloride.

The reaction is uniform only when the minimum quantity of acid indicated above is present, but it ought not to exceed $\frac{1}{3}$ the volume, and the precautions before given as to the action of hydrochloric acid on permanganate must be taken into account, hence it is preferable to use bichromate as follows:—

Kessler (Poggend. Annal. 118, 17,) has carefully experimented upon this method and adopts the following processes.

A standard solution of arsenious acid is prepared containing 5 gm. pure acid, dissolved by the aid of sodic hydrate, neutralized with hydrochloric acid, 100 c.c. concentrated hydrochloric acid added, then diluted with water to 1 litre; each c.c. of this solution contains 0·005 gm. As^2O^3 and represents exactly 0·007374 gm. Sb^2O^3.

Solutions of potassic bichromate and ferrous sulphate of known strength in relation to each other, are prepared in the usual way and a freshly prepared solution of potassic ferricyanide used as indicator.

The relation between the bichromate and arsenious solution is und by measuring 10 c.c. of the latter into a beaker, 20 c.c. drochloric acid of sp. gr. 1·12 and from 80 to 100 c.c. of water, insure uniformity of action the volume of HCl. must never be s than $\frac{1}{6}$ or more than $\frac{1}{3}$), the bichromate solution is then added excess, the mixture allowed to react for a few minutes and the rous solution added until the indicator shows the blue colour; to ke the exact point more closely, $\frac{1}{2}$ or 1 c.c. bichromate solution y be added, and again iron, until the precise ending is obtained.

The Analytical process with Antimony. The material free from ganic matter, organic acids, or heavy metals, is dissolved in the per proportion of hydrochloric acid and titrated precisely as t described for the arsenious solution; the strength of the hromate solution having been found in relation to As^2O^3 the culation as respects Sb^2O^3 presents no difficulty. Where direct ration is not possible the same course may be adopted as with enic, § 56.2, namely precipitation with H^2S and digestion with rcuric chloride.

In the case of using permanganate it is equally necessary to have same proportion of HCl. present in the mixture, and the ndard solution must be added till the rose colour is permanent. e permanganate may be safely used with $\frac{1}{4}$ the volume of HCl ordinary temperatures, and as the double tartrate of antimony d potassium can readily be obtained pure, and the organic acid ercises no disturbing effect in the titration, it is a convenient terial upon which to standardize the solution.

Distillation of Antimonious or Antimonic Sulphide with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen (Schneider).

When either of the sulphides of antimony are heated with drochloric acid in Bunsen's, Fresenius', or Mohr's distilling paratus, fig. 23, or 32, for every 1 eq. of antimony present as lphide, 3 eq. of sulphuretted hydrogen are liberated. If, therefore, the latter be estimated, the quantity of antimony is ascertained. The process is best conducted as follows:—

The antimony to be determined is brought into the form of ter- or pentasulphide (if precipitated from a hydrochloric solution, tartaric acid must be previously added, to prevent the precipitate being contaminated with chloride), which, together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The absorption tube, contains a mixture of caustic soda or potash, with a definite quantity of $\frac{N}{10}$ arsenious acid solution, § 34 in sufficient excess to retain all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, acidified with hydrochloric acid, to precipitate all the arsenious sulphide. The whole is then diluted to, say 300 c.c., and 100 c.c. taken with a pipette, neutralised with sodic carbonate, some bicarbonate added, and the titration for excess of arsenious acid performed with $\frac{N}{10}$ iodine and starch, as directed in § 34.

GOLD.

Au = 196·5.

1 c.c. or 1 dm. normal oxalic acid = 0·0655 gm. or 0·655 grn. gold.

§ 59. The technical assay of gold for coining purposes is invariably performed by cupellation. Terchloride of gold is, however, largely used in photography and electro gilding, and, therefore, it may be necessary sometimes to ascertain the strength of a solution of the chloride or its value as it occurs in commerce.

If to a solution of gold in the form of chloride (free from nitric acid), an excess of oxalic acid be added, in the course of from 18 to 24 hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate, the amount of gold will be obtained.

Example: A 15 grain tube of the chloride of gold of commerce was dissolved in water, and the solution made up to 300 decems. 20 dm. of normal oxalic acid were then added, and the flask set aside for twenty-four hours in a warm place, at the end of that time the gold had settled, and the supernatant liquid was clear and colourless. 100 dm. were taken out with a pipette, and titrated with $\frac{N}{10}$ permanganate, of which 25 dm. were required; this multiplied by 3 gives 75 dm.=7·5 dm. normal oxalic acid, which deducted from the 20 dm. originally added, left 12·5 dm.; this multiplied by $\frac{1}{3}$ the equivalent of gold (1 eq. of gold chloride decomposing 3 eq. oxalic acid) = 0·655 gave 8·195 grn. metallic gold or multiplied by 101 (=$\frac{1}{3}$ eq. $Au.\ Cl^3$) gave 12·625 grn.; either way the result was 84 per cent. of chloride of gold instead of 100.

SILVER.

Ag.=108.

1 c.c. or 1 dm. $\frac{N}{10}$ solution of sodic chloride=0·0108 gm. or 0·108 grn. metallic silver; also 0·0171 gm. or 0·171 grn. silver nitrate.

Decinormal Sodic Chloride Solution.—See Sect. 35. 2.

Decinormal Silver Solution.—See Sect. 35. 1.

§ 60. The determination of silver is precisely the converse of the operations described under chlorine, § 36, 1 and 2, and the process may either be concluded by adding the sodic chloride till no further precipitate is produced, or potassic chromate may be used as an indicator. In the latter case, however, it is advisable to add the salt solution in excess, then a drop or two of chromate solution, and titrate residually with $\frac{N}{10}$ silver solution, till the red colour is produced, for the excess of sodic chloride.

1. Analysis of the Silver Solutions used in Photography.

The silver bath solutions for sensitising collodion and paper frequently require examination, as their strength is constantly lessening. To save calculation, it is better to use an empirical solution of salt than the systematic one described above.

This is best prepared by dissolving 43 grains of pure sodic chloride in 10,000 grains of distilled water; each decem (=10 grs.) of this solution will precipitate 0·125 grn. (*i.e.* $\frac{1}{8}$ grn.) of pure silver nitrate; therefore, if 1 fluid drachm of any silver solution be taken for examination, the number of decems of salt solution required to precipitate all the silver will be the number of grains of silver nitrate in each ounce of the solution.

Example: One fluid drachm of an old nitrate bath was carefully measured into a stoppered bottle, 10 or 15 drops of pure nitric acid and a little distilled water added; the salt solution was then cautiously added, shaking well after each addition until no furt precipitate was produced; the quantity required was 26·5 dm.= grains of silver nitrate in each ounce of solution.

Crystals of silver nitrate may also be examined in the same w by dissolving say 30 or 40 grs. in an ounce of water, taking drachm of the fluid and titrating as above.

In consequence of the rapidity and accuracy with which sil may be determined, when potassic chromate is used as indica some may prefer to use that method. It is then necessary to h a standard solution of silver, of the same chemical power as salt solution; this is made by dissolving 125 grains of pure dry neutral silver nitrate in 1,000 dm. of distilled water; b solutions will then be equal, volume for volume.

Suppose, therefore, it is necessary to examine a silver solut used for sensitising paper. One drachm is measured, and if free acid be present, cautiously neutralise with a weak solut of sodic carbonate; 100 dm. of salt solution is then added wit pipette, if the solution is under 100 grs. to the ounce, the quan will be sufficient. 3 or 4 drops of chromate solution are t added, and the silver solution delivered from the burette until red colour of silver chromate is just visible. If 25·5 dm. h been required, that number is deducted from the 100 dm. salt solution, which leaves 74·5 dm., or 74½ grains to ounce.

This method is much more likely to give exact results in hands of persons not expert in analysis than the ordinary plan precipitation, inasmuch as with collodion baths, containing as t always do silver iodide, it is almost impossible to get the sup natant liquid clear enough to distinguish the exact end of analysis.

2. Estimation of Silver, in Ores and Alloys, by Starch Iodi
(Method of Pisani and F. Field.)

If a solution of blue starch iodide be added to a neu solution of silver nitrate, while any of the latter is in excess blue colour disappears, the iodine entering into combination w the silver; as soon as all the silver is thus saturated, the b colour remains permanent, and marks the end of the process; reaction is very delicate, and the process is more especially applica to the analysis of ores and alloys of silver containing lead copper, but not mercury, tin, iron, manganese, antimony, arsenic, or gold in solution.

The solution of starch iodide, devised by Pisani, is made by rubbing together in a mortar 2 gm. iodine with 15 gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask, and digesting in a water-bath for about an hour, or until it has assumed a dark bluish-gray colour; water is then added till all is dissolved. The strength of the solution is then ascertained by titrating it with 10 c.c. of a solution of silver containing 1 gm. in the litre, to which a portion of pure precipitated calcic carbonate is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch solution should be of such a strength that about 50 c.c. is required for 10 c.c. of the silver solution (=0·01 gm. silver).

F. Field (Chem. News, vol. ii. p. 17), who discovered the principle of this method simultaneously with Pisani, uses a solution of iodine in potassic iodide with starch liquor. Those who desire to make use of this plan can use the deci- and centinormal solutions of iodine described in § 32, the results being the same in either case.

In the analysis of silver containing copper the solution must be considerably diluted in order to weaken the colour of the copper, a small measured portion is then taken, calcic carbonate added, and starch iodide till the colour is permanent. It is best to operate with about from 60 to 100 c.c., containing not more than 0·02 gm. silver; when the quantity is much greater than this, it is preferable to precipitate the greater portion with $\frac{N}{10}$ sodic chloride, and to complete with starch iodide after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid, and filter off the lead sulphate, then add calcic carbonate to neutralise excess of acid, filter again if necessary, then add fresh carbonate and titrate as above.

8. Assay of Commercial Silver (Plate, Bullion, Coin, &c.), Gay Lussac's Method modified by J. G. Mulder.

For more than thirty years Gay Lussac's method of estimating silver in its alloys has been practised intact, at all the European mints, under the name of the "humid method," in place of the old system of cupellation; during that time it has been regarded as one of the most exact methods of quantitative analysis; the researches of Mulder, however, into the innermost details of the process have shown that it is capable of even greater accuracy than has hitherto been gained by it. For the particulars of Mulder's investigations I cannot do better than refer the reader to the excellent translations of his memoir, contributed to the "Chemical News," by Adriani.

The principle of the process is the same as described under the head of chlorine, depending on the affinity which that body has for silver in preference to all other substances, and resulting in the formation of chloride of silver, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrious inventor of this process for assaying silver and which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established, it is the best plan of procedure; if, therefore, a standard solution of salt be made of such strength that 100 c.c. will exactly precipitate 1 gramme of silver, it is manifest that each $\frac{1}{10}$ c.c. will precipitate 1 milligramme or $\frac{1}{1000}$th part of the gramme taken, and consequently in the analysis of 1 gramme of any alloy containing silver, the number of $\frac{1}{10}$ c.c. required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner, consequently a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 c.c. will exactly precipitate 1 gramme of silver, and, therefore, 1 c.c. one milligramme.

The silver alloy to be examined (the composition of which must be approximately known), is weighed so that about 1 gramme of pure silver is present, it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 c.c. of standard solution of salt added from a pipette in order to precipitate exactly 1 gm. of silver, the bottle containing the mixture is then well shaken until the chloride of silver has curdled, leaving the liquid clear.

The question is now—Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate be produced, 1 c.c. is delivered in, and after clearing, another, and so on as long as a precipitate is produced; if on the other hand the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 gm., a decimal solution of silver is used, prepared by dissolving 1 gm. pure silver in pure nitric acid and diluting to 1 litre, this solution is added after the same manner as the salt solution just described, until no further precipitate occurs; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 gm. of the alloy.

The process thus shortly described is that originally devised by ay Lussac, and it was taken for granted that when equivalent hemical proportions of silver and sodic chloride were brought thus contact that every trace of the metal was precipitated from the lution, leaving sodic nitrate and free nitric acid only in solution. he researches of Mulder, however, go to prove that this is not rictly the case, but that when the most exact chemical proportions silver and salt are made to react on each other, and the chloride s subsided, a few drops more of either salt or silver solution will oduce a further precipitate, indicating the presence of both silver trate and sodic chloride in a state of equilibrium, which is upset the addition of either salt or silver. Mulder decides, and no ubt rightly, that this peculiarity is owing to the presence of sodic trate, and varies somewhat with the temperature and state of lution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, til no further precipitate appears, the clear liquid will at this int give a precipitate with dilute silver solution, and if it be added ll no further cloudiness is produced, it will again be precipitable dilute salt solution.

Example: Suppose that in a given silver analysis the decimal lt solution has been added so long as a precipitate is produced, d that 1 c.c. (=20 drops of Mulder's dropping apparatus) of cimal silver is in turn required to precipitate the apparent excess, would be found that when this had been done, 1 c.c. more of salt lution would be wanted to reach the point at which no further oudiness is produced by it, and so the changes might be rung time ter time; if, however, instead of the last 1 c.c. (=20 drops) of lt, half the quantity be added, that is to say 10 drops ($= \frac{1}{2}$ c.c.); ulder's so-called neutral point is reached, namely, that in which, the liquid be divided in half, both salt and silver will produce e same amount of precipitate. At this stage the solution contains silver chloride dissolved in sodic nitrate, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

1. By adding decimal salt solution until it just ceases to produce a cloudiness.

2. By adding a slight excess of salt, and then decimal silver till no more precipitate occurs.

3. By finding the neutral point.

According to **Mulder** the latter is the only correct method, and preserves its accuracy at all temperatures up to 56° C. (=133° Fahr.) while the difference between 1 and 3 amounts to $^1/_2$ a milligramme, and that between 1 and 2 to 1 milligramme on 1 gramme of silver at 16° C. (=60° Fahr.) and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by **Mulder's** method than by that of **Gay Lussac**, but as a compensation, much greater accuracy is obtained.

On the whole, it appears to me preferable to weigh the alloy so that slightly more than 1 gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of a precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation—say 100·1 c.c. are found equal to 1 gm. of silver, the operator has only to calculate that quantity of the salt solution in question for every 1 gm. of silver he assays in the form of alloy, and the error produced by the solubility of silver chloride in sodic nitrate is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 17° C.=62° Fahr., this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment, for it requires a great expenditure of time and patience to reverse an assay two or three times, and each time cautiously adding the solutions, drop by drop, then shaking and waiting for the liquid to clear, beside the risk of discolouring the chloride of silver, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 gm. pure silver, then it is best to add once for all 2, 3, or 5 c.c., according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

The Standard Solutions and Apparatus.

(*a.*) **Standard Salt Solution.** Pure sodic chloride is prepared by treating a concentrated solution of the whitest table salt first with a solution of caustic baryta to remove sulphuric acid and magnesia, then with a slight excess of sodic carbonate to remove baryta and lime, warming and allowing the precipitates to subside; then evaporating to a small bulk, that crystals may form; these are separated by a filter, and slightly washed with cold distilled water; dried, removed from the filter, and heated to dull redness, and when cold preserved in a well-closed bottle for use. The mother liquor is thrown away or used for other purposes. Of the salt so prepared, or of chemically pure rock-salt (Steinsalz, a substance to be obtained freely in Germany), 5·4145 gm. is to be weighed and dissolved in 1 litre of distilled water at 16° C. =60° Fahr. 100 c.c. of this solution will precipitate exactly 1 gm. silver; it is preserved in a well-stoppered bottle, and shaken before use.

(*b.*) **Decimal Salt Solution.** 100 c.c. of the above solution is diluted to exactly 1 litre with distilled water at 16° C.=60° Fahr. 1 c.c. will precipitate 0·001 gm. of silver.

(*c.*) **Decimal Silver Solution.** Pure metallic silver is best prepared y galvanic action from pure chloride; and as clean and secure a ethod as any, is to wrap a lump of clean zinc, into which a silver ire is melted, with a piece of wetted bladder or calico, so as to ep any particles of impurity contained in the zinc, from the silver. he chloride is placed at the bottom of a porcelain dish, covered ith dilute sulphuric acid, and the zinc laid in the middle; the lver wire is bent over so as to be immersed in the chloride; as on as the acid begins to act upon the zinc, the reduction commences in the chloride, and grows gradually all over the mass; the sulting finely-divided silver is well washed, first with dilute acid, en with hot water, till all acid and soluble zinc are removed.

The moist metal is then mixed with a little sodic carbonate, ltpetre, and borax, say about an eighth part of each, and dried rfectly.

The metallic silver obtained as above is never free altogether om organic matter and undecomposed chloride, and, therefore, it must invariably be melted. Mulder recommends that the melting should be done in a porcelain crucible; immersed in sand contained in a common earthen crucible; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the silver when melted no particles of dirt or sand may fall into it. If the quantity of metal be small it may be melted in a porcelain crucible over a gas blowpipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe-clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a goldsmith's mill, in order that it may be readily cut for weighing; the granulated metal is, of course, ready for use at once without any rolling.

1 gm. of this silver is dissolved in pure dilute nitric acid and diluted to 1 litre; each c.c. contains 0·001 gm. silver; it should be kept from the light.

(*d.*) **Dropping Apparatus for concluding the assay.** Mulder constructs a special affair for this purpose, consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid, the delivery tube has an opening of such size that 20 drops measure exactly 1 c.c.—the vessel itself is not graduated. As this arrangement is of more service to assay than to general laboratories, it need not be further described here. A small burette divided in $\frac{1}{10}$ c.c. with a convenient dropping tube, will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100 c.c. pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 gm. of distilled water at 16° C.

The test bottles, holding about 200 c.c., should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be covered over the stopper.

(*e.*) **Titration of the standard Salt Solution.** From what has been said previously as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt, containing 5·4145 gm. per litre, although this is chemically rect in its strength. The real working power must be found experiment. From 1·002 to 1·004 gm. of absolutely pure silver weighed on the assay balance, put into a test bottle with about .c. of pure nitric acid, about 1·2 sp. gr., and gently heated in water or sand bath till it is all dissolved. The nitrous vapours then blown from the bottle, and it is set aside to cool down to ut 16° C. or 60° Fahr.

he 100 c.c. pipette, which should be securely fixed in a support, ıen carefully filled with the salt solution, and delivered into test bottle contained in its case, the moistened stopper inserted, red over with the black velvet or cloth, and shaken con- ›usly till the chloride has clotted and the liquid becomes clear; topper is then slightly lifted, and its point touched against the of the bottle to remove excess of liquid, again inserted, and particles of chloride washed down from the top of the bottle ırefully shaking the clear liquid over them. The bottle is then ght under the decimal salt burette, and ½ c.c. added, the mix- shaken, cleared, another ½ c.c. put in, and the bottle lifted y out of its case to see if the precipitate is considerable; r, 2 or 3 drops only of the solution are added at a time until urther opacity is produced by the final drop. Suppose, for ınce, that in titrating the salt solution it is found that 1·003 gm. lver require 100 c.c. concentrated, and 4 c.c. decimal solution, ether equal to 100·4 c.c. concentrated, then—

$$1{\cdot}003 \text{ silver} : 100{\cdot}4 \text{ salt} :: 1{\cdot}000 : x \quad x = 100{\cdot}0999.$$

result is within $\frac{1}{10000}$ of 100·1, which is near enough for the ›ose, and may be more conveniently used. The operator, efore, knows that 100·1 c.c. of the concentrated salt solution 6° C., will exactly precipitate 1 gm. silver, and calculates rdingly in his examination of alloys.

ı the assay of coin and plate of the English standard, namely, silver and 0·9 copper, the weight corresponding to 1 gm. silver 081 gm., therefore, in examining this alloy 1·085 gm. may be hed.

'hen the quantity of silver is not approximately known, a minary analysis is necessary, which is best made by dissolving 1 gm. of the alloy in nitric acid, and precipitating very care- with the concentrated salt solution from a $\frac{1}{10}$ c.c. burette. pose that in this manner 1 gm. of alloy required 45 c.c. salt tion,

100·1 salt : 1·000 silver : : 45 : x $x = 0·4495$, and again
0·4495 : 1 : : 1·003 : $x = 2·231$.

2·231 gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

Assaying on the Grain System.

It will be readily seen that the process just described may quite as conveniently be arranged on the grain system by substituting 10 grains of silver as the unit in place of the gramme, each decem of concentrated salt solution would then be equal to $\frac{1}{10}$th of a grain of silver, and each decem of decimal solution to $\frac{1}{100}$th of a grain.

IODINE.

$I = 127$.

Free and Combined.

1 c.c. $\frac{N}{10}$ hyposulphite $= 0·0127$ gm. Iodine.
„ „ $= 0·0166$ gm. Potassic iodide.

1. By Distillation.

§ 61. FREE iodine is of course very readily estimated by solution in potassic iodide, and titration with starch and $\frac{N}{10}$ hyposulphite, as described in § 32.*

Combined iodine, in haloid salts, such as the alkaline iodides, must be subjected to distillation with hydrochloric acid, and some other substance capable of assisting in the liberation of free iodine, which is received into a solution of potassic iodide, and then titrated with $\frac{N}{10}$ hyposulphite in the ordinary way. Such a substance presents itself best in the form of ferric oxide, or some of its combinations; if, therefore, hydriodic acid, or what amounts to the same thing, an alkaline iodide, be mixed with an excess of ferric oxide, and distilled in the apparatus shown in figs. 23, or 32, the following reaction occurs:—

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* I would here again impress upon the operator's notice that it is of great importance to ascertain the exact strength of the standard solutions of iodine and hyposulphite as compared with each other. Both solutions constantly undergo an amount of change depending upon the temperature at which they are kept, their exposure to light, &c., and therefore it is absolutely necessary, to ensure exactness in the multifarious analyses which can be made by the aid of these two reagents, to verify their agreement by weighing a small portion of pure dry iodine at intervals, and titrating it with the standard hyposulphite.

$$Fe^2O^3 + 2IH = 2FeO + H^2O + I^2.$$

The best form in which to use the ferric oxide is the double sulphate of ferric oxide and ammonia or potash (iron alum).

The iodide and iron alum being brought into the little flask, fig. 23, sulphuric acid, of about 1·3 sp. gr. or so, is added, and the cork carrying the still tube inserted. This tube is not carried into the solution of potassic iodide in this special case, but within a short distance of it, and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube, and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be present in sufficient quantity to absorb it all. When no more violet vapours are to be seen in the flask, the operation is ended; but to make sure, it is well to empty the ioduretted solution of odine out of the condensing tube into a beaker, and put a little resh iodide solution with starch in, then heat the flask again; the lightest traces of iodine may then be discovered by the occurrence f the blue colour. In case this occurs, the distillation is connued a little while, then both liquids mixed, and titrated with $\frac{N}{10}$ hyposulphite as usual.

Ferric chloride may be used instead of the iron alum, but it must be free from nitric acid or active chlorine, (best prepared rom dry Fe^2O^3 and HCl).

The analysis may be checked by titrating the ferrous oxide in he retort with $\frac{N}{10}$ permanganate or bichromate.

2. Oxidation of combined Iodine by Chlorine, (Golfier Besseyre and Dupré.)

This wonderfully sharp method of estimating iodine depends upon its conversion into iodic acid by free chlorine. When a solution of potassic iodide is treated with successive quantities of chlorine water, first iodine is liberated, then chloride of iodine (ICl) formed; if starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue while any of the others will be coloured intense violet; a further addition of chlorine, in sufficient quantity, produces pentachloride of iodine (ICl^5), or rather, as water is present, iodic acid (IO^3H); no coloration of the above substances are produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Besseyre and Dupré, independently of each other for the purpose of estimating iodine. The former suggested the use of starch, the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

Examples: 30 c.c. of weak chlorine water were put into a beaker with potassic iodide and starch, then titrated with $\frac{N}{100}$ hyposulphite, of which 17 c.c. were required.

10 c.c. of solution of potassic iodide, containing 0·010 gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared; the quantity used was 85·8 c.c. The excess of chlorine was then ascertained by adding sodic bicarbonate, potassic iodide, and starch; a slight blue colour occurred; this was removed by $\frac{N}{100}$ hyposulphite, of which 1·2 c.c. were used. Now, as 30 c.c. of the chlorine solution required 17 c.c., the 85·8 c.c. required 48·62 c.c. of hyposulphite: from this, however, must be deducted the 1.2 c.c. in excess, leaving 47·42 c.c. $\frac{N}{100}$ = 4·742 c.c. of $\frac{N}{10}$ hyposulphite, which multiplied by 0·00211, the one-sixth of $\frac{1}{10000}$ eq. (1 eq. of iodic acid liberating 6 eq. iodine), gave 0·010056 gm. iodine instead of 0·01 gm.

Mohr suggests an improvement upon this method, which dispenses with the use of chloroform, or other similar agent.

The weighed iodine compound is brought into a stoppered flask, and chlorine water delivered from a large burette in excess, that is, until all yellow colour has disappeared; a drop of the mixture brought in contact with a drop of starch liquor produces no blue colour; sodic bicarbonate is then added till the mixture is neutral or slightly alkaline, together with potassic iodide and starch; the blue colour is then removed by $\frac{N}{100}$ hyposulphite; the strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 0·010108 gm. iodine, instead of 0·01 gm.

3. Oxidation by Permanganate, (Reinige.)

This process for estimating iodine in presence of bromides and chlorides gives satisfactory results.

When potassic iodide and permanganate are mixed, the rose colour of the latter disappears, a brown precipitate of manganic peroxide results, and free potash with potassic iodate remain in solution. 1 eq. I = 127 reacts on 1 eq. $K^2Mn^2O^8 = 316$, thus—

$$KI + K^2Mn^2O^8 = KIO^3 + K^2O + 2MnO^2.$$

Heat accelerates the reaction, and it is advisable, especially with weak solutions, to add a small quantity of potassic carbonate to increase the alkalinity. No organic matter must be present.

The permanganate and hyposulphite solutions required in the rocess may conveniently be of $\frac{N}{10}$ strength, but their reaction upon ach other must be definitely fixed by experiment as follows— c.c. of permanganate solution are freely diluted with water, a w drops of sodic carbonate added, and the hyposulphite added in ry small portions until the rose colour is just discharged; the ght turbidity produced by the precipitation of hydrated manganic ide need not interfere with the exact point.

The Analytical process: The iodine compound being dissolved water, and always existing only in combination with alkaline or rthy bases, is heated to gentle boiling, rendered alkaline with lic or potassic carbonate, and permanganate added till in distinct cess, best known by removing the liquid from the fire, for minute, when the precipitate will subside, leaving the upper uid rose coloured; the whole may then be poured into a 0 c.c. flask, cooled, diluted to the mark, and 100 c.c. ken out for titration with hyposulphite; the amount so used ing multiplied by 5, will give the proportion required for the hole liquid, whence can be calculated the amount of iodine. prove the accuracy of the process in a mixture of iodides, omides, and chlorides, with excess of alkali, the following experient was made. 7 gm. commercial potassic bromide, the same of dic chloride, with 1 gm. each of potassic hydrate and carbonate, re dissolved in a convenient quantity of water, and heated to iling; permanganate was then added cautiously to destroy the ces of iodine and other impurities affecting the permanganate so ng as decoloration took place; the slightest excess showed a en colour (manganate); to the mixture was then added 0·1246 . pure iodine, and the titration continued as described; the sult was 0·125 gm. I. With systematic solutions of permangate and hyposulphite, the calculation is as follows:—

$$\text{I c.c. } \tfrac{N}{10} \text{ solution} = 0·0127 \text{ gm. I.}$$

4. By Nitrous Acid and Carbon Bisulphide, (Fresenius.)

This process requires the following standard solutions:—

(*a*) Potassic iodide, about 5 gm. per litre.

(*b*) Sodic hyposulphite, $\frac{1}{20}$ normal, 12·4 gm. per litre or thereabout.

(*c*) Nitrous acid, prepared by passing the gas into tolerably strong sulphuric acid until saturated.

(*d*) Pure carbon bisulphide.

(*e*) Solution of sodic bicarbonate made by dissolving 5 gm. of the salt in 1 litre of water, and adding 1 c.c. hydrochloric acid.

The strength of the sodic hyposulphite in relation to iodine is first ascertained by placing 50 c.c. of the iodide solution into a 50.0 c.c. stoppered flask, then about 150 c.c. water, 20 c.c. carbon bisulphide, then dilute sulphuric acid, and lastly, 10 drops of the nitrous solution; the stopper is then replaced, and the whole well shaken, set aside to allow the carbon liquid to settle, and the supernatant liquid poured into another clean flask; the carbon bisulphide is then treated three or four times successively with water in the same way till the free acid is mostly removed, the washings being all mixed in one flask; 10 c.c. of bisulphide are then added to the washings, well shaken, and if at all coloured, the same process of washing is carried on; finally the two quantities of bisulphide are brought upon a moistened filter, washed till free from acid, a hole made in the filter, and the bisulphide which now contains all the iodine in solution allowed to run into a clean small flask, 30 c.c. of the sodic bicarbonate solution added, then brought under the hyposulphite burette, and the solution allowed to flow into the mixture while shaking until the violet colour is entirely discharged. The quantity of hyposulphite so used represents the weight of iodine contained in 50 c.c. of the standard potassic iodide, and may be used on that basis to ascertain any unknown weight contained in a similar solution.

When very small quantities of iodine are to be titrated, weaker solutions and smaller vessels may be used.

5. By $\frac{N}{10}$ Silver Solution and Starch Iodide, (Pisani.)

The details of this process are given under the head of silver assay, § 60.2, and are of course simply a reversal of the method *there given*.

CHLORINE.

Cl = 35·5.

'HE estimation of chlorine in combination as chlorides has ›en described in § § 26, 36, 37, and therefore needs not ;her discussed, except perhaps, to mention that in using lelicate reaction between silver and potassic chromate, as care should be taken to use only very small quantities of (at the most three drops of saturated solution), and to . of the absence of chlorine in the chromate itself.

›istillation and subsequent Titration with Hyposulphite.

›s where chlorine is evolved direct in the gaseous form representative of some other body, (see § 33,) a very absorption apparatus is shewn in fig. 33, the little flask 33
a is used as the distilling vessel, connected with the bulb tubes by an india-rubber joint; the stoppers for the tubes are also of the same material, the whole of which should be cleansed from sulphur by boiling in weak alkali. A fragment of solid magnesite may with advantage be added to the acid liquid in the distilling flask, in all other respects the process is conducted exactly as is described in § 33.

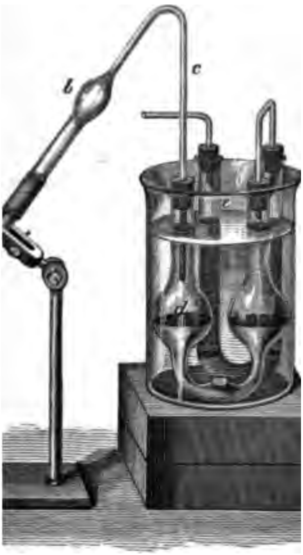

Fig. 33.

pparatus is equally well adapted to the absorption of or other gases, and possesses the great recommendation › is scarcely a possibility of regurgitation.

Chlorine Gas and Hypochlorites or Bleaching Compounds.

1 c.c. $\frac{N}{10}$ arsenious or hyposulphite solution = 0·00355 gm. Cl.
1 litre of Chlorine at 0° C., and 0·76 m.m., weighs 3·17 gm.

Chlorine water can be titrated with hyposulphite by adding a measured quantity of it to a solution of potassic iodide, then delivering the hyposulphite from a burette till the colour of the free iodine has disappeared; or by using an excess of the reducing agent, then starch liquor, and titrating residually with $\frac{N}{10}$ iodine. When arsenious solution is used for titration, the chlorine water is delivered into a solution of sodic carbonate, excess of arsenic added, then starch liquor and $\frac{N}{10}$ iodine till the colour appears, or the iodised starch paper may be used, § 34. p. 80.

Bleaching Powder. The chief substance of importance among the compounds of hypochlorous acid is the so-called chloride of lime, used in very large quantities for bleaching purposes. The estimation of the free chlorine contained in it presents no difficulty when arsenious solution is used for titration.

Commercial bleaching powder consists of a mixture in variable proportions of calcic hypochlorite (the true bleaching agent), calcic chloride, and hydrate; and in some cases the preparation contains considerable quantities of chlorate, due to imperfect manufacture; in such cases Bunsen's method of analysis gives inaccurate results, the chlorate being recorded as a bleaching agent, whereas it is not so; it is generally valued and sold in this country by its percentage of chlorine. In France it is sold by degrees calculated from the volume of gaseous chlorine: 100° French = 31·78% English.

2. Estimation by Arsenious Solution.

The first thing to be done in determining the value of a sample of bleaching powder is to bring it into solution, which is best managed as follows:—

The sample is well and quickly mixed, and 10 gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a litre flask, the sediment again rubbed with water, poured off, and so on repeatedly until the whole of the chloride has been conveyed into the flask without loss, and the mortar washed quite clean; the flask is then filled to the mark with water, well shaken, and 100 c.c. of the milky liquid taken out with a pipette, emptied into a beaker, and the $\frac{N}{10}$ arsenious solution delivered in from a burette until a drop of the mixture taken out with a glass rod, and brought in contact with the prepared starch paper, § 34, gives no blue stain.

The starch paper may be dispensed with by adding arsenious solution in excess, then starch liquor, and titrating residually with $\frac{N}{10}$ iodine till the blue colour appears, the number of c.c. of arsenic used, multiplied by the factor 0·00355, will give the percentage of chlorine.

Example: 100 c.c. of chloride of lime liquid prepared as above directed were put into a beaker, and 86 c.c. of arsenious solution added, then starch liquor and 1·5 c.c. of $\frac{N}{10}$ iodine to produce the blue colour = 84·5 c.c. of arsenious solution, which multiplied by 0·00355 gave 0·2999; and as 1 gm. of the sample was contained in the 100 c.c., 29·99 per cent of chlorine.

Another 100 c.c. was carefully titrated with arsenious solution by the aid of iodised starch paper. 84·5 c.c. were required, also equal to 29·99%. Some recommend that the mixture of chloride of lime and water should be allowed to stand till clear, and the clear liquid only used for titration; but this invariably gives lower results than when the milky mixture is used.

By weighing 3·55 gm. of the sample, and diluting to 1 litre; then taking 100 c.c. for titration, the number of c.c. of arsenious solution required will be the percentage of chlorine direct.

A more rapid method can be adopted in cases where a series of samples have to be tested as follows—4·95 gm. pure arsenious acid are finely powdered and dissolved by the aid of a gentle heat in about 15 c.c. of glycerine, then diluted with water to 1 litre; 25 c.c. are measured into a flask and 1 c.c. of indigo solution added. The turbid solution of bleaching powder is poured into a suitable burette, and before it has time to settle is delivered with constant shaking into the blue arsenious solution until the colour is just discharged; the percentage of chlorine is then found by a slight calculation.

3. Bunsen's Method.

10 or 20 c.c. of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of potassic iodide added; the mixture is then diluted somewhat, acidified with hydrochloric acid, and the liberated iodine titrated with $\frac{N}{10}$ hypo-

sulphite and starch, 1 eq. iodine so found represents 1 eq. chlorine.

This is an exceedingly ready method of estimating chlorine, but in cases where calcic chlorate is present, it records the chlorine in it, as well as that existing as hypochlorite; but as the chlorate is of no value in bleaching, it is always preferable to analyse bleaching powder by means of arsenious solution. The amount of chlorate can always be found by taking the difference between the two methods.

BROMINE.

$Br = 80$.

§ 63. This element can be estimated precisely in the same way as chlorine by $\frac{N}{10}$ silver solution § 36, or alkalimetrically as in § 26, but these methods are seldom of any avail since the absence of chlorine or its combinations is a necessary condition of accuracy.

A process for the estimation of bromine in presence of chlorine is still much wanted in the case of examining kelp liquors, &c. **Heine** (Journ. f. pract. Chem. 36, 184,) uses a colorimetric method in which the bromine is liberated by free chlorine, absorbed by ether, and the colour compared with an ethereal solution of bromine of known strength. **Fehling** states that with care the process gives fairly accurate results. It is of course necessary to have an approximate knowledge of the amount of bromine present in any given solution.

Reimann (Annal. d. Chem. u. Pharm. 115, 140,) adopts the following method, which gives tolerably accurate results; but requires skill and practice.

The neutral bromine solution is placed in a stoppered vessel together with a globule of chloroform about the size of a hazelnut. Chlorine water of known strength is then added cautiously from a burette, protected from bright light, in such a way as to insure first the liberation of the bromine, which colours the chloroform orange yellow; then more chlorine water until the yellowish white colour of chloride of bromine occurs ($KBr + 2Cl = KCl + BrCl$.)

The operation may be assisted by making a weak solution of potassic chromate of the same colour as a solution of chloride of bromine in chloroform, to serve as a standard of comparison.

The strength of the chlorine water is ascertained by potassic iodide and $\frac{N}{10}$ hyposulphite. 2 eq. $Cl = 1$ eq. Br.

In examining mother liquors containing organic matter, they must be evaporated to dryness in presence of free alkali, ignited, extracted with water; then neutralized with hydrochloric acid before titrating as above described.

CHLORATES, IODATES, AND BROMATES.

Chloric anhydride, $Cl^2O^5=151$. Iodic anhydride, $I^2O^5=334$.
Bromic anhydride, $Br^2O^5=240$.

§ 64. The compounds of chloric, iodic, and bromic anhydrides may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective anhydrides taken as monobasic, or their compounds, liberate 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while iodous and bromous chlorides remain in the retort. In both these cases digestion is preferable to distillation.

Example: 0·2043 gm. pure potassic chlorate, equal to the sixth part of $\frac{1}{10000}$ eq., was decomposed by digestion with potassic iodide and strong hydrochloric acid in the bottle shown in fig. 24; after the reaction was complete, and the bottle cold, the stopper was removed, and the contents washed out into a beaker; starch added, and 103 c.c. $\frac{N}{10}$ hyposulphite delivered in from the burette; then again 28·2 c.c. of $\frac{N}{100}$ iodine solution, to reproduce the blue colour; this latter was therefore equal to 2·32 c.c. $\frac{N}{10}$ iodine, which deducted from the 103 c.c. hyposulphite gave 100·68 c.c., which multiplied by the factor 0·002043, gave 0·2056 gm. instead of 0·2043 gm.

CYANOGEN.

CN = 26.

1 c.c. $\frac{N}{10}$ silver solution = 0·0052 gm. Cyanogen.
" " = 0·0054 gm. Hydrocyanic acid.
" " = 0·01302 gm. Potassic cyanide.
" iodine = 0·003255 gm. Potassic cyanide.

1. By Standard Silver Solution (Liebig).

§ 65. THIS ready and accurate method of estimating cyanogen in prussic acid, alkaline cyanides, &c., was discovered by Liebig, and is fully described in the "Ann. der Chemie und Pharm.," vol. lxxvii. p. 102. It is based on the fact, that when a solution of silver nitrate is added to an alkaline solution containing cyanogen, with constant stirring, no permanent precipitate of silver cyanide occurs until all the cyanogen has combined with the alkali and the silver, to form a soluble double salt; (in the presence of potash, for example, KCy, AgCy.) If the slightest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of silver cyanide occurs, the double compound being destroyed. If, therefore, the silver solution be of known strength, the quantity of cyanogen present is easily found; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination, that, when sodic chloride is present, no permanent precipitate of silver chloride occurs until the quantity of silver necessary to form the compound is slightly overstepped.

In all cases the solution to be titrated must be rendered alkaline, if not already so. Essential oil of bitter almonds, or its spirituous solution, need generally the addition of a quantity of strong spirit to prevent turbidity, from the separation of the essential oil, which would otherwise interfere with the delicacy of the reaction.

When no alkali is present, it is still possible to titrate a solution containing cyanogen with silver; but in this case the precipitate of silver cyanide appears at once, and double as much silver is required as when alkali is present. When the titration is conducted in this manner, the manipulations are precisely the same as with the determination of chlorine by silver, the silver solution being added, with constant shaking, until no further precipitate occurs. Liebig's method is, however, preferable.

Example with Hydrocyanic Acid: In order that each c.c. or dm. of $\frac{N}{10}$ silver solution should represent 1 per cent. of anhydrous acid, it would be necessary to take 0·54 c.c. or dm. for the analysis, but this is too little to measure with accuracy, it is better to take ten times this quantity = 5·4 c.c. or dm.; if the number of c.c. or dm. of silver solution required to produce the turbidity be divided by 10, or the decimal point moved one place to the left, the figures will represent the percentage of real prussic acid present.

5·4 c.c., therefore, of the so-called Scheele's hydrocyanic acid was carefully taken with a pipette, mixed with a small quantity of solution of potash, and titrated with $\frac{N}{10}$ silver, of which 42·5 c.c. were required; the quantity of real acid contained in the sample was 4·25%.

5·4 dm. of the *Acid. Hydrocy. dil. P. L.* were titrated as above and 19 dm. $\frac{N}{10}$ silver required = 1·9%.

54 dm. *Aq. Lauro Cerasi* titrated as above required 9·5 dm., the strength was therefore 0·095%, the decimal point being removed two places to the left, as 100 times the quantity was taken.

Caution.—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with silver nitrate, into the upper end, so as to avoid the danger of inhaling any of the acid, otherwise it is decidedly preferable to weigh it.

Example with Potassic Cyanide: The quantity of this substance necessary to be taken for analysis, so that each c.c. or dm. shall be equal to 1 per cent. of the pure cyanide, is 1·30 gm. or 13·0 grn.; 13 grains, therefore, of the commercial article were dissolved in water, no further alkali being necessary, and 54 dm. $\frac{N}{10}$ silver required to produce the permanent turbidity; the sample, therefore, contained 54% of real cyanide.

The large quantities of this material used at the present time in electro-plating and photography render it frequently desirable to ascertain its chemical strength.

2. By Iodine (Fordos and Gelis).

This process, which is principally applicable to alkaline cyanides, depends on the fact that when a solution of iodine is added to one of potassic cyanide the iodine loses its colour so long as any undecomposed cyanide remains. The reaction may be expressed by the following formula:—

$$CyK + 2I = IK + ICy.$$

Therefore, 2 eq. iodine represent 1 eq. cyanogen in combination; so that 1 c.c. of $\frac{N}{10}$ iodine expresses the half of $\frac{1}{10000}$ eq. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonate alkalies, which would equally destroy the colour of the iodine as the cyanide, consequently these must l converted into bicarbonates, best done by adding carbonic ac water (ordinary soda water).

Example: 5 gm. potassic cyanide were weighed and dissolve in 500 c.c. water, then 10 c.c. (=0·1 gm. cyanide) taken with pipette, diluted with about ¼ litre of water, 100 c.c. of soda wat added, then $\frac{N}{10}$ iodine delivered from the burette until the solutic possessed a slight but permanent yellow colour, 25·5 c.c. we required, which multiplied by 0·003255 gave 0·08300 gm., instea of 0·1 gm. or 83°/$_{0}$ real cyanide. Sulphides must of course l absent.

FERRO- AND FERRICYANIDES.

Potassic Ferrocyanide.

$$K^4Cy^6Fe + 3H^2O = 422.$$

Metallic iron × 7·541 = Crystallised potassic ferrocyanid
Double iron salt × 1·077 = „ „ „

1. Oxidation to Ferricyanide by Permanganate, (De Haen.)

§ 66. This substance may be estimated by potassic perma ganate, which acts by converting it into red prussiate. The p cess is easy of application, and the results accurate. A standa solution of pure ferrocyanide should be used as the basis up which to work, but can, however, be dispensed with, if the operat choose to calculate the strength of his permanganate upon iron its compounds. If the permanganate is decinormal, there is course very little need for calculation (1 eq. = 422 must be us as the systematic number, and therefore 1 c.c, of $\frac{N}{10}$ permangan is equal to 0·0422 gm of yellow prussiate). The standard soluti of pure ferrocyanide contains 20 gm. in the litre; each c.c. w contain 0·020 gm.

The Analytical process: 10 c.c. of the standard prussi solution are put into a white porcelain dish or beaker standing white paper, and 250 c.c. or so of water added; it is then acidifi pretty strongly with sulphuric acid, and the permanganate deliver from the burette until a pure uranium yellow colour appea it is then cautiously added until the faintest pink tinge occu De Haen, Fresenius, and Mohr all agree in stating t the end of the reaction is hindered by turbidity; this I ha not found to be the case, but have invariably found t when the solution of ferrocyanide is very dilute, say ¼ gm. 250 or 300 c.c. water freely acidified, and the operation p formed in a clean white evaporating basin, that the mixture remains clear, and the end is very exactly shown; a drop or two in excess of permanganate being sufficient to give the necessary pinkish tinge. I attribute the different experience obtained by us to the fact, that I invariably use pure permanganate of potash for titration, and sulphuric instead of hydrochloric acid.

Potassic ferrocyanide may be estimated, when mixed with sulphocyanide, by standard solution of cupric sulphate, the whole of the ferrocyanogen being carried down in combination with the copper; the ending of the titration may be found by bringing a drop of the liquid in contact with a drop of ferric chloride on filter paper. If alkaline sulphides be present, the solution should be boiled with lead carbonate, filtered, acidified with sulphuric acid, then titrated with the copper solution.

POTASSIC FERRICYANIDE.

$$K^6Cy^{12}Fe^2 = 658.$$

Metallic iron	× 5·88	= Potassic ferricyanide.
Double iron salt	× 1·68	= ,, ,,
$\frac{N}{10}$ Hyposulphite	× 0·0329	= ,, ,,

1. By Iodine and Hyposulphite.

This salt can be estimated either by reduction to ferrocyanide and titration with permanganate or bichromate as above, or by Lenssen's method, which is based upon the fact, that when potassic iodide and ferricyanide are mixed with tolerably concentrated hydrochloric acid, iodine is set free.

$$K^6Fe^2Cy^{12} + 2KI = 2K^4Cy^6Fe + I^2.$$

the quantity of which can be estimated by $\frac{N}{10}$ hyposulphite and starch liquor; this method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions. C. Mohr's modification (see Zinc, § 45.1) is, however, more reliable, and is as follows:—The ferricyanide is dissolved in a convenient quantity of water, potassic iodide in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure zinc sulphate in excess; after standing a few minutes to allow the decomposition to perfect itself, the excess of acid is neutralised by sodic carbonate, so that the latter slightly predominates.

At this stage all the zinc ferricyanide first formed is converted

into the ferrocyanide of that metal, and an equivalent quantity o
iodide set free, which can at once be titrated with $\frac{N}{10}$ hyposulphit
and starch, and with very great exactness. 1 c.c. $\frac{N}{10}$ hyposulphit
= 0·0329 gm. potassic ferricyanide.

The mean of five determinations made by **Mohr** gave 100·2
instead of 100.

2. Reduction of Ferri- to Ferrocyanide.

This process is, of course, necessary when the determination b
permanganate has to be made, and is best effected by boiling th
weighed ferricyanide with an excess of potash or soda, and addin
small quantities of concentrated solution of ferrous sulphate unti
the precipitate which occurs possesses a blackish colour (signifyin
that the magnetic oxide is formed); the solution is then dilute
to a convenient quantity, say 300 c.c., well mixed and filtere
through a dry filter; 50 or 100 c.c. can then be taken, sulphuri
acid added, and titrated with permanganate as before described.

Other soluble ferro- or ferricyanides can be examined in the sam
way as the potassium salts, and if insoluble, they may generall
be converted into the latter by boiling with strong caustic potas

SULPHUR.

S = 32.

Estimation in Pyrites, Ores, Residues, &c.

1. Alkalimetric Method (Pelouze).

§ 67. THIS process, which is more especially designed for t
rapid estimation of sulphur in iron and. copper pyrites, is susce
tible of very tolerable accuracy, the greatest variation from t
truth not exceeding 1 or 1½%, when the manipulation is careful
performed.

The principle of the process is based on the fact, that wh
sulphur is ignited with potassic chlorate and sodic carbonate, t
sulphur is converted by oxidation entirely into sulphuric aci
which expels its equivalent proportion of carbonic acid from t
soda, forming neutral sodic sulphate; if, therefore, an accurate
weighed quantity of the substance be fused with a known weig
of pure sodic carbonate in excess, and the resulting mass titrat
with normal acid, to find the quantity of unaltered carbonate, t

proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate, and that actually required after the ignition.

For the sake of avoiding calculation, it is advisable to take 1 gm. of the finely levigated pyrites, and 5·3 gm. of pure sodic carbonate for each assay; and as 5·3 gm. of sodic carbonate represent 100 c.c. of normal sulphuric acid (= 4·0 gm. SO^3), it is only necessary to subtract the number of c.c. used after the ignition from 100, and multiply the remainder by the factor 0·016 (1 c.c. of normal acid being equal to 0·016 gm. of S), in order to arrive at the weight of sulphur in the 1 gm. of pyrites, and by moving the decimal point two places to the right, the percentage of that substance is obtained.

Example: Some cubes of iron pyrites were broken, and a small portion very finely powdered in a hardened steel mortar.

1 gm. of the powder was mixed *intimately* with 5·3 gm. of pure sodic carbonate, and about 7 gm. each of potassic chlorate, and decrepitated sodic chloride, in powder (the latter is added for the purpose of moderating the action); the whole was then introduced into a platinum crucible, and gradually exposed to a dull red heat for ten minutes; the crucible was then suffered to cool somewhat, and warm distilled water added; the solution so obtained was drawn off with a pipette and brought on a moistened filter, the process repeated five or six times, the residue then emptied into a beaker and boiled with a large quantity of water, the whole brought on the filter, and thoroughly washed with boiling water till all soluble matter was removed; the clear filtrate was then coloured with litmus, and titrated as in § 16. 67 c.c. of normal acid were required, which deducted from 100, left 33 c.c.; this multiplied by 0·016 gave 0·528 gm. or 52·8°/ of sulphur; pure FeS^2 contains 53·3°/₀.

The insoluble ferric oxide remaining on the filter was dissolved in hydrochloric acid, reduced with zinc, and titrated with bichromate, as in § 31, yielding 46·5°/₀ of iron.

If pure sodic carbonate is not at hand, the ordinary commercial article will answer the purpose, but the quantity of normal acid necessary to saturate it must of course be previously found. An iron spoon or ladle may also be used instead of the platinum crucible.

If roasted pyrites are to be examined by this method, it is unnecessary to add the salt, and equal quantities of the substance, sodic carbonate and potassic chlorate, may be taken for the combustion.

Kolb (Journ. de Pharm. et de Chim. ser. iv, vol. x, p. 401) has experimented very fully upon Pelouze's process, as descr above, and found the sources of error to be various—formatio ferric sulphate, loss of chlorine, sulphur chloride, &c. The pr recommended in its place, and which appears to be satisfac consists in mixing sodic carbonate and cupric oxide with the fi powdered ore and igniting the mixture in an iron, copper, or plati vessel to a low red heat for about 15 minutes; the whole of sulphur is oxidised to sulphuric acid, and combines quietly wit soda; the remaining unchanged sodic carbonate is then estim by titration as usual. The method seems particularly appli to roasted pyrites, the details being as follows:—

From 5 to 10 gm. of the ore, according to its richness in sul (if more than 10 per cent. 5 gm., less than 10 per cent. 10 gm. weighed and intimately mixed with 5 gm. of sodic carbonate, about 50 gm. of dry cupric oxide, placed in the crucible, and he over a small gas flame with frequent stirring for 12 or 15 min the heat never exceeding a low red; the crucible is then co the contents treated with hot water, filtered, and the filtrate washings titrated with normal acid as usual.

2. By Oxidation and subsequent Titration with Standar Baric Chloride.

The estimation of sulphur by barium has recently been investigated by Teschemacher, Denham Smith, Holl and others, (Chem. News, xxiv, 61; xxvii, 16,) the results of w shew that owing to the tendency which baric sulphate has to taminate itself with other matters when precipitated from m solutions, and the varying solubility of the precipitate in solutions, a careful volumetric method is far preferable to the mation by weight. The experiments carried out by Teschema and Smith especially shew that the composition of the precip varies with the nature and amount of other substances pre and that its solubility in excess of hydrochloric acid is greater than is usually thought possible. Further, that method of purification of the sulphate by fusion, or treat with reagents, is worse than all. From my own exper of sulphur estimations with barium by weight, carried o years in gas testing, and the valuation of ores for sulphuric manufacture, I am quite willing to endorse the words of experimenters, "that the estimation of sulphur and sulphuric by the weight of baric sulphate obtained is, and can be, co only by accident, and when the adherent impurity happens exactly to counterbalance the baric sulphate dissolved."

The conditions insisted upon by **Teschemacher** and **Smith** are as follows:—

The use of a standard solution of baric chloride by weight.

The complete oxidation of the sulphur, and subsequent expulsion of all the nitric acid.

The absence of a large excess of hydrochloric acid.

The use of moderate quantities of solutions.

The use of considerable weights of pyrites in testing, thus avoiding the extreme of multiplication of any analytical error in the percentage return.

Grain weights are used in the examples given, but operators can of course easily adopt corresponding weights in grammes, if desired. With respect to the use of a standard solution of baric chloride by weight, the only advantage gained by it is that the operation is independent of temperature; by working at ordinary temperatures with graduated instruments of known correctness, and in exact correspondence with each other, there cannot be much scope for error, and therefore it matters little which course is adopted, but a considerable saving of time and trouble is gained by using the burette instead of the balance.

(*a*) **Standard Solution of Baric Chloride.** The best substance for fixing the strength of the solution of baric chloride was found to be ferrous sulphate, pure light green crystals of which are crushed to the size of hemp seed, freed from any powder by sifting, then washed repeatedly with small quantities of spirit of wine, (methylated spirit may be used,) finally air-dried on bibulous paper, and preserved in well closed bottles.

108·6 grains of this salt are equal to 12·5 grains of sulphur (= 91·02 grains of baric sulphate) and it possesses the advantage of yielding the same kind of solution as actually occurs in the analysis of pyrites.

For convenience of calculation the baric solution is adjusted so that exactly 1000 grains by weight shall represent 25 grains of sulphur; the usual Spanish or Norwegian pyrites contain on the average 47 to 50 °/₀ of sulphur, hence, if 25 grains of the sample be taken for analysis, it will require between 470 and 500 grains of standard solution to precipitate all the sulphuric acid produced by the oxidation of the ore. The solution of baric chloride is made by dissolving the pure crystals in distilled water, to which a small proportion of hydrochloric acid is added, to prevent the formation of baric carbonate, which is apt to occur in a neutral solution if kept for any length of time.

(*b*) **Standard Solution of Sulphuric Acid.** This solution is made to correspond volume for volume with the baric solution.

The actual working power of the baric solution may be found by taking 1000 grains of it, heating to near boiling, and adding it to a boiling solution of dilute sulphuric acid in moderate excess. The precipitate of baric sulphate so obtained is collected on a filter as usual, and after ignition yields mere traces of chlorine when treated with water; the process must not, however be reversed, otherwise an impure precipitate occurs. The final trial is best made with ferrous sulphate, 108·6 grains (= 12·5 grs. S) of which are dissolved in about 1000 grains (= 100 dms.) of water slightly acidulated with hydrochloric acid, and heated nearly to boiling; to this is added 490 to 495 grains of the baric solution, also hot, stirring well, and finally boiling rapidly in a platinum or porcelain basin; a small portion is then filtered, and the standard baric solution added drop by drop to the filtrate, which must be returned to the test liquor, and boiled at each testing until a filtrate is obtained, which, after standing, just gives a cloud with both baric chloride and sulphuric acid solutions.

Since some trouble and time are required to fix the exact value of the standard baric solution, it is advisable to prepare some quantity at a time, and to preserve it in a cool place, in separate well stoppered bottles.

The Analytical process with Pyrites: The sample is first carefully selected, powdered, and thoroughly mixed, then in small quantity brought to an impalpable powder by grinding in an agate mortar. 200 grains are taken and dried at 100° C., after which about 30 grains are weighed and placed in a flask of about 20 ozs. capacity. The ore is then oxidised with 300 grains weight of *aqua regia*, to which 200 grains of hydrochloric acid are added. When the energetic action ceases the whole is evaporated *just* to dryness, a point which demands care and watchfulness to hit. 100 grains more hydrochloric acid are then added to the flask to redissolve the contents. If any unoxidised sulphur can be perceived by the eye after treatment with HCl, the test must be rejected, and another oxidation commenced with 25 grs. of more finely powdered ore.

A small flask holding some 1000 grains of standard solution, with dropping tube, is now counterpoised, and so much of the solution transferred to a porcelain basin as practice shows may be looked for as nearly equivalent to the strength of pyrites in sulphur. The contents of the basin are next heated nearly to boiling, and poured into the test solution of the pyrites, then the whole is returned to the basin from the flask, and the latter washed out with a small quantity of water. The liquid is then boiled rapidly, and a small damped filter being in readiness, a little of the mixed solution is filtered, and a portion of the filtrate added to about 3 or 4 grs. of standard barium solution placed from the counterpoised flask in a test-glass. Should a further precipitate be produced, this tested solution is to be returned to the basin with the rest of the filtrate, and so much more solution of barium added as may be judged requisite. This is again boiled and filtered, using the same filter, and tested as before, this operation being repeated until a precipitate ceases to appear with the barium solution, when the weight of the solution employed is taken and noted. It frequently happens that when the operation is complete, both barium and dilute sulphuric acid show a cloudiness in the filtrate after the lapse of a few minutes. When this is the case, the precipitation has been successfully conducted.

It is stated that by the method above described the amount of sulphur in pyrites may be determined with accuracy and certainty to $\frac{1}{10}$th per cent., and that in execution it will be found more simple and expeditious than the old gravimetric method.

P. Holland has obtained good results in estimating sulphur only by fusing the very finely powdered dried ore with ten times its weight of an equal mixture of dry sodic carbonate and potassic nitrate. The operation may be conducted in a large platinum crucible, heated strongly over a Bunsen burner, or in a hard glass combustion tube, about 6 in. long, and half an inch internal diameter, connected by a cork and delivery tube dipping into water in a flask. Should any products of combustion in their escape carry over sulphates or sulphuric acid, they are retained by the water; the tube is finally heated with a powerful flame, and when cold, the broken tube and contents emptied into the flask, the delivery tube rinsed into the mixture, the fused mass dissolved in slight excess of hydrochloric acid, ammonia added till a slight precipitate of ferric oxide appears, then as much hydrochloric acid and water added as are necessary to bring the fluid to the conditions under which the baric solution was standardized. With 1 gm. of pyrites and 200 c.c. total volume of solution, 2 c.c. of free acid is a convenient quantity.

3. Estimation of Sulphur in Coal Gas.

A most convenient and accurate process for this estimation is that of Wildenstein, § 40.2. The liquid produced by burning the measured gas in a Letheby or Vernon Harcourt apparatus well mixed, and brought to a definite volume; a portion repr senting a known number of cubic feet of gas is then poured into glass, porcelain, or platinum basin, acidified slightly with HC heated to boiling, and a measured excess of standard baric chlori added; the excess of acid is then cautiously neutralized wit ammonia, (free from carbonate,) and the excess of barium asce tained by standard potassic chromate exactly as described i § 40, p. 97.

The usual method of stating results is in grains of sulphur p 100 cubic feet of gas. This may be done very readily by usin semi-normal solutions of baric chloride and potassic chromate o the metric system, and multiplying the number of c.c. of bar solution required with the factor 0·1234, which at once gives th amount of sulphur in English grains.

Standard solutions can of course be made in the same manner o the grain system.

4. Estimation of Alkaline Sulphides by Standard Zinc Solution.

This method, which is simply a counterpart of § 45,3, is esp cially applicable for the technical determination of alkali sulphides in impure alkalies, mother liquors, &c.

If the zinc solution be made by dissolving 3·253 gm. of pu metallic zinc in hydrochloric acid, supersaturating with ammoni and diluting to a litre, or 32·53 grn. to 1000 dm. 1 c.c. or d will respectively indicate—

0·0016 gm.	or 0·016 grn.	Sulphur
0·0039 „	or 0·039 „	Sodic sulphide
0·00551 „	or 0·0551 „	Potassic sulphide
0·0034 „	or 0·034 „	Ammonic sulphide.

The zinc solution is added from a burette until a drop, broug in contact with the lead solution on filtering paper, no long gives a black stain at the edge.

5. Sulphurous Acid and Sulphites.

Solutions of sulphurous acid are very readily titrated by iodin as described in § 32, but it is necessary to remember that in ord to secure the proper reaction as defined by Bunsen, the soluti must not contain more than 0·05 per cent. of sulphur dioxide. Mohr, however, has found that the difficulty as to concentration is overcome by the use of ammonic, potassic, or sodic bicarbonate (see § 32, note,) which have no effect on starch iodide.

1 c.c. $\frac{N}{10}$ iodine = 0·0032 gm. SO^2.

SULPHURETTED HYDROGEN.

$H^2S = 34.$

1 c.c. $\frac{N}{10}$ arsenious solution = 0·00255 gm. H^2S.

1. By Arsenious Acid (Mohr).

§ 68. THIS residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine, as devised by Dupasquier. The principle is based on the fact, that when sulphuretted hydrogen is brought into contact with an excess of arsenious acid in hydrochloric acid solution, arsenic sulphide is formed; 1 eq. of arsenious acid and 3 eq. of sulphuretted hydrogen produce 1 eq. of arsenic sulphide and 3 eq. of water,

$$As^2O^3 + 3H^2S = As^2S^3 + 3H^2O.$$

The excess of arsenious acid used is found by $\frac{N}{10}$ iodine and starch, as in § 34. In the case of estimating the strength of sulphuretted hydrogen water, the following plan may be pursued.

A measured quantity, say 10 c.c. of $\frac{N}{10}$ arsenious solution, is put into a 300 c.c. flask, and 20 c.c. of sulphuretted hydrogen water added, well mixed, and sufficient hydrochloric acid added to produce a distinct acid reaction; this produces a precipitate of arsenic sulphide and the liquid itself is colourless. The whole is then diluted to 300 c.c., filtered through a dry filter into a dry vessel, 100 c.c. of the filtrate taken out and neutralized with sodic bicarbonate, then titrated with $\frac{N}{10}$ iodine and starch, as in § 34; the quantity of arsenious acid so found is deducted from the original 10 c.c., and the remainder multiplied by the requisite factor for sulphuretted hydrogen.

The estimation of sulphuretted hydrogen contained in coal gas, can by this method be made very accurately by leading the gas through the arsenious solution, or still better, through a dilute solution of caustic alkali, then adding arsenious solution, and titrating as before described. The apparatus devised by Mohr for this purpose is arranged as follows. The gas from a common burner is led by means of a vulcanised tube into two successive small wash bottles, containing the alkaline solution;

from the last of these it is led into a large **Woulf's** bottle fille with water; the bottle has two necks, and a tap at the bottom, or of the necks contains the cork through which the tube carryir the gas is passed; the other, a cork through which a good-size funnel with a tube reaching to the bottom of the bottle is passed when the gas begins to bubble through the flasks, the tap is opene so as to allow the water to drop rapidly; if the pressure of gas strong, the funnel tube acts as a safety valve, and allows the wat to rise up into the cup of the funnel; when a sufficient quantit of gas has passed into the bottle, say six or eight pints, the wat which has issued from the tap into some convenient vessel, measured into cubic inches or litres, and gives the quantity of ga which has displaced it. In order to insure accurate measuremen all parts of the apparatus must be tight.

The flasks are then separated, and into the second 5 c.c. c arsenious solution placed, and acidified slightly with hydrochlori acid; if any traces of a precipitate occur it is set aside for titratio with the contents of the first flask, into which 10 c.c. or so c arsenious solution are put, acidified as before, both mixed togethe diluted to a given measure, filtered, and a measured quantit titrated as before described.

2. By Permanganate (Mohr).

If a solution of sulphuretted hydrogen is added to a dilute solu tion of ferric sulphate, the ferric salt is reduced to the ferrou state, and free sulphur separates, the ferrous salt so produced ma be measured accurately by permanganate without removing th separated sulphur. Ferric sulphate, free from ferrous compound in sulphuric acid solution, is placed in a stoppered flask, and th solution of sulphuretted hydrogen added to it with a pipette; th mixture is allowed to stand half-an-hour or so, then diluted co siderably, and permanganate added until the rose colour appears.

$$56\ Fe = 17\ H^2S$$

or each c.c. of $\frac{N}{10}$ permanganate represents 0·0017 gm. of H^2S.

3. By Iodine.

Sulphuretted hydrogen in mineral waters can be accurate estimated by iodine in the following manner:—

10 c.c. or any other necessary volume of $\frac{N}{100}$ iodine solution a measured into a 500 c.c. flask, and the water to be examined add until the colour disappears. 5 c.c. of starch liquor are then adde and $\frac{N}{100}$ iodine until the blue colour appears, the flask is then fill

to the mark with pure distilled water. The respective volumes of iodine and starch solution, together with the added water, deducted from the 500 c.c. will shew the volume of water actually titrated by the iodine; a correction should be made for the excess of iodine necessary to produce the blue colour.

Fresenius examined the sulphur water of the Grindbrunnen, in Frankfurt a. M. (Zeitschrift f. an. chem. xiv, 321) both volumetrically and by weight for H^2S with very concordant results. 361·44 gm. of water (correction for blue colour being allowed) required 20·14 c.c. of iodine solution, 20·52 c.c. of which contained 0·02527 of free iodine $= H^2S$ 0·009194 gm. per million. 444·65 gm. of the same water required, under the same conditions, 25·05 c.c. of the same iodine solution $= H^2S$ 0·009244 gm. per million. By weight the H^2S was found to be 0·009377 gm. per million.

PHOSPHORIC ACID AND PHOSPHATES.

$P^2O^5 = 142.$

§ 69. The estimation of phosphoric acid, either volumetrically or by weight, presents a subject of considerable interest, and one which has taxed the ingenuity of most chemists. The present enormous consumption of artificial manures throughout the civilized world, the agricultural value of which depends to a large extent upon the amount of phosphoric acid contained in them, and the state of combination in which it exists, has led to the suggestion of many processes for its estimation, and has probably given rise to more controversy than any other substance of commercial interest in existence.

Moreover, it is one of the subjects which has given scope for a large amount of quackery among so-called commercial analysts, some of whom seem to arrogate to themselves secret methods of analysis, which render their services valuable on the one hand to the buyer, or on the other to the seller of phosphatic materials, because they can certify to either low or high results as the case may be.

The anxiety of dealers to obtain certain results suitable to their pockets can hardly be surprising, when it is considered that a difference of 1 per cent. may make a variation in price of hundreds of pounds in one transaction; nevertheless, in this case, as also in the valuation of soda ash and caustic soda by analysis, such anomalies should at once and for ever be got rid of by uniform action on the part of honest analysts, who above most men should

have the object before them of stating the exact truth, so f
lies in their power.

It is to be hoped that the Committee on this and kind
jects, appointed by the Chemical Section of the British Ass
will help to accomplish this uniformity when their Re
issued.

In this treatise I have nothing to do with gravimetric p
for the estimation of phosphoric acid, except in so far
serve to verify the results obtained by volumetric methods,
these latter I am of opinion that one only is admissible—
that by uranium; this opinion is based upon many hund
analyses conducted in my own laboratory, and upon the te
of many competent chemists who have occupied themselv
the matter, and whose contributions to various scientific j
have been consulted and freely used in the compilation
section.*

1. By Precipitation as Uranic Phosphate in Acetic Acid S

This method is based on the fact that when uranic ni
acetate is added to a neutral solution of tribasic phosphor
such, for instance, as sodic orthophosphate, the whole
phosphoric acid is thrown down as yellow uranic phosphat
$P^2O^5 + Aq.$; should the solution, however, contain free
acid, it must be neutralized with an alkali, and an alkaline
added, together with excess of free acetic acid; in case o
ammonia and ammonic acetate, the whole of the phospho
is thrown down as double phosphate of uranium and an
having a light lemon colour, and the composition 2(
$2NH^4O,P^2O^5 + Aq.$ When this precipitate is washed w
water, dried and burned, the ammonia is entirely dis
leaving uranic phosphate, which possesses the formula 2(
P^2O^5, and contains in 100 parts 80·09 uranic oxide an

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* Fresenius' Quant. Chem. Analyse, 6te Aufl., p. 411.
Abesser, Jani u. Märcker, Zeitschr. Chem. An. xii, 239.
Schumann, ibid. xi, 382; Janovsky, ibid. xi, 153.
Gilbert, ibid. xii, 1; Rümpler, ibid. xii, 151.
Fresenius, Neubauer, and Luck, ibid. ix, 16.
Mohr, Titrirbuch, 4te Aufl., 520.
Neubauer, Anal. des Harns, 6te Aufl.
Joulie, Moniteur Scientifique, 1872–3, et Annuaire de la Pharmaci par Dr. C. Mehu, 1875, p. 465, etc., etc.

phosphoric acid. In the presence of fixed alkalies, instead of ammonia, the precipitate consists simply of uranic phosphate. By this method phosphoric acid may be completely removed from all the alkalies and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the gravimetric process were fully described by me in the Chemical News, (vol. 1, pp. 97, 122) and immediately after the publication of that article, while employed in further investigation of the subject, I devised the volumetric method now to be described. Since that time it has come to my knowledge that Neubauer* and Pincus† had independently of each other and myself, arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that of measure, when the delicate reaction between uranium and potassic ferrocyanide is known. Moreover, the great want of a really good volumetric process for phosphoric acid in place of those hitherto used, has been felt by all who have anything to do with it, and consequently the most would be made of any new method possessing so great a claim to accuracy as the gravimetric estimation of phosphoric acid by uranium undoubtedly does.

The great advantages possessed by the method over Liebig and Raewsky's iron process are that the combination between the phosphoric acid and uranium is definite and certain, and that the mixture needs no filtration, since uranic phosphate produces no colour with potassic ferrocyanide, like ferric phosphate. For the ready determination of phosphoric acid in certain manures and urine, the process is exceedingly accurate.

2. Estimation of Phosphoric Acid in combination with Alkaline Bases, or in presence of small quantities of Alkaline Earths.

The necessary materials are—

(*a*) A standard solution of uranium.

(*b*) A standard solution of tribasic phosphoric acid.

(*c*) A solution of sodic acetate in dilute acetic acid, made by dissolving 100 gm. of sodic acetate in water, adding 100 c.c. of pure acetic acid of sp. gr. 1·04, and diluting to 1 litre; exact quantities are not necessary.

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* Archiv. für wissenschäftliche Heilkunde, Bd. iv, p. 228.

† Journal für Prakt. Chem., 76, 104.

(*d*) A freshly prepared solution of potassic ferrocyanide, or some finely powdered pure crystals of the same salt.

The uranium solution may consist either of uranic nitrate, or acetate dissolved in distilled water, and of such strength that 1 c.c. represents about 5 milligrammes of phosphoric acid. An approximate solution is obtained by using about 40 gm. of either salt to the litre. The solution should be perfectly clear and free from basic salt. Experience has shown that the most concordant results are invariably obtained by uranic acetate, since the presence of ammonia (as in the case of urine), slightly but sensibly affects the production of the colour between uranium and potassic ferrocyanide, when uranic nitrate is used; if, however, uranic acetate is not at hand the standard uranic nitrate solution must be titrated in the presence of an ammoniacal salt. In standard solutions made from either uranic nitrate or acetate, it is advisable to add about 25 c.c. of pure glacial acetic, or a corresponding quantity of weaker acid to each litre of solution—exposure to light has then no reducing action.

3. Titration of the Uranium Solution.

When the uranium solution is not required for manures, it may be titrated upon sodic phosphate as follows,—10·085 gm. of the crystallized, non-effloresced salt (previously powdered and pressed between bibulous paper to remove any adhering moisture), are weighed, dissolved in water, and diluted to 1 litre. 50 c.c. of this solution should represent 0·1 gm. P^2O^5; but as it is difficult to obtain sodic phosphate in a normal state of hydration, it is always advisable to check it by evaporating 50 c.c. of the solution to dryness, in a small platinum basin, or crucible, and igniting at a strong heat. The sodic pyrophosphate so remaining should weigh 0·1874 gm.

50 c.c. of this solution are measured into a small beaker; 5 c.c. sodic acetate solution added, and the mixture heated to 90° or 100°C. The uranium solution is then delivered in from a burette, divided into $\frac{1}{10}$ c.c. until a test taken, shall shew the slight predominence of uranium—this is done by spreading a drop or two of the hot mixture upon a clean white level plate, and bringing in contact with the middle of the drop, a small glass rod moistened

with the solution of ferrocyanide, or a dust of the powdered salt —the occurrence of a faint brown tinge shews an excess of uranium, the slightest amount of which produces a brown precipitate of uranic ferrocyanide.

A second or third titration is then made in the same way, so as to arrive exactly at the strength of the uranium solution, which is then diluted and re-titrated, until exactly 20 c.c. are required to produce the necessary reaction with 50 c.c. sodic phosphate.

Suppose 18·7 c.c. of the uranium solution have been required to produce the colour, with 50 c.c. of phosphate solution, then every 18·7 c.c. will have to be diluted to 20 c.c. in order to be of the proper strength—or 187 to 200, or 935 to 1000. After dilution, two or three fresh trials must be made to insure accuracy.

It is of considerable importance that the actual experiment for estimating phosphoric acid by means of the uranium solution should take place with about the same bulk of fluid that has been used in standardizing the solution, and with as nearly as possible the same relative amount of sodic acetate, and the production of the same depth of colour in testing. If these conditions are observed, the method is really capable of extreme accuracy. Hence the proportions here recommended have been chosen, so that 50 c.c. of liquid shall contain 0·1 gm. P^2O^5, which is about the proportion that would naturally occur in the usual course of analysis.

A little practice enables the operator to tell very quickly the precise point, but it must be remembered that when the two drops are brought together for the production of the chocolate colour, however faint it seems at first, if left for some little time, the colour increases considerably, owing to the retarding action of the sodic acetate and acetic acid upon the formation of uranic ferrocyanide, but this has no effect upon the accuracy of the process, since the original standard of the solution has been based on an experiment conducted in precisely the same way.

The Analytical process: In estimating unknown quantities of phosphoric acid, it is necessary to have an approximate knowledge of the amount in any given material, so as to fulfil as nearly as possible the conditions laid down above, that is to say, 50 c.c. of solution shall contain about 0·1 gm. P^2O^5, or whatever other proportion may have been used in standardizing the uranium solution. It is found that considerable variations in the amount of sodic acetate and acetic acid modify the ending of the process to a noticeable extent; on the other hand, if the operation be conducted with approximate volumes of liquid and amounts of substance, very concordant results are obtained, and I do not hesitate to say that with care and practice, the estimation of phosphoric acid, in combination with alkaline or earthy bases, by this method, is fully as accurate as any method of estimation by weight.

The compound containing the phosphoric acid to be estimated is dissolved in water, or in the least possible quantity of acetic acid, 5 c.c. of sodic acetate added, and the volume made up to about 50 c.c., then heated, and the uranium solution delivered in cautiously, with frequent testing as above described, until the faint brown tinge appears.

The first trial will give roughly the amount of phosphoric acid present, and taking that as a guide, the operator can vary the amount of liquid and sodic acetate for the final titration, should the proportions be found widely differing from those under which the strength of the uranium was originally fixed.

Each c.c. of uranium solution = 0·005 gm. P^2O^5.

4. Estimation of Phosphoric Acid in combination with Lime and Magnesia, (Bones, Bone Ash, Soluble Phosphates, and other Phosphatic Materials, free from Iron and Alumina.)

The procedure in these cases differs from the foregoing in two respects only—that is to say, the uranium solution is preferably standardized by tribasic calcic instead of sodic phosphate, and in the process of titration it is necessary to add nearly the full amount of uranium required before heating the mixture, so as to prevent the precipitation of calcic phosphate, which is apt to occur in acetic acid solution: or the modification adopted by Fresenius, Neubauer, and Luck, may be used, which consists in reversing the process by taking a measured volume of uranium in excess, and delivering into it the solution of phosphate until a drop of the mixture ceases to give a brown colour with ferrocyanide; this plan gives, however, much more trouble, and possesses no advantage on the score of accuracy, because in any case at least two titrations must occur, and the first being made somewhat roughly, in the ordinary way, shews within 1 or 2 c.c. the volume of standard uranium required, and in the final trial it is only necessary to add at once nearly the quantity, then heat the mixture, and finish the titration by adding a drop or two of uranium at a time until the required colour is obtained.

It is not safe to depend upon the usual preparations of tri-calcic phosphate by weighing any given quantity direct, owing to uncertainty as to the state in which the phosphoric acid may exist;

therefore, in order to titrate the uranium solution with calcic phosphate, it is only necessary to take a convenient quantity of precipitated well washed tri-calcic phosphate, and dissolve it in a slight excess of dilute nitric acid; by this means is obtained a solution of acid monocalcic phosphate: in order to ascertain the exact amount of phosphoric acid present in a given measure of this solution, it must be diluted to a definite volume, a measured portion placed in a platinum capsule or crucible, ammonia added in slight excess, the liquid evaporated to dryness, then ignited to dispel the ammonic nitrate, and the resulting tri-calcic phosphate immediately cooled and weighed; its composition is $Ca^3P^2O^8 = 310$ representing $P^2O^5 = 142$; from these numbers it is of course easy to calculate the amount of phosphoric acid in any given volume of the solution.

Example: 50 c.c. of such a solution were evaporated and ignited, then found to weigh 0·2713 gm. = P^2O^5 0·12427 gm. 50 c.c. of the same solution were then treated with ammonic molybdate, and the phosphoric acid carefully estimated with ammoniated magnesic chloride; it yielded $Mg^2P^2O^7$ 0·1942 gm. = P^2O^5 0·12429 gm.: 50 c.c. of the same solution were then titrated with uranium solution, previously standardized on pure calcic phosphate, and of such strength that 1 c.c. = 0·00522 gm. P^2O^5, the volume required was 23·8 c.c. = 0·12424 gm. P^2O^5. These numbers agree very closely, and greater concordance cannot be expected.

It is hardly necessary to say that in preparing a quantity of standard uranium solution the greatest care must be taken, by checking its working power in various ways. It is agreed by all operators that there exists no more accurate method of estimating phosphoric acid by weight than as magnesic pyrophosphate, using magnesic chloride instead of sulphate in preparing the precipitant, adding it in slight excess only at a moderate temperature, and allowing the mixture to stand from three to four hours; the precipitate is then collected on a filter, washed with the smallest quantity of ammoniacal water necessary to remove all traces of chlorine, (no correction need be made for washings,) the filter dried, that and the precipitate ignited separately, first at a moderate, and finally at a very strong heat; the latter is especially requisite when the precipitate is collected from molybdic solution.

Another method equally exact, and according to my experience less troublesome, is the direct precipitation in acetic acid solution, by uranic acetate, (alumina and iron of course being absent, small quantities of iron may be allowed,) and weighing as uranic phosphate; the liquid should be well boiled after the addition of uranium, (when traces of iron are present, a few drops of uranous chloride should be added,) poured into a large beaker, filled up with boiling water, and allowed to stand till quite clear, the clear liquid removed by a syphon flask, the beaker again filled with boiling water, again removed when clear; the same should be done a third time, when the precipitate may be brought on the filter, and needs very little further washing.

It is useless to try to filter this precipitate unless it is first freely washed by decantation, and as it is absolutely insoluble in water, large quantities may be used without fear. Conducted in this way, the estimation need not occupy more than four or five hours. Fuller details of this process are contained in my paper previously mentioned, (Chem. News, vol. i, pp. 97. 122.)

Either of the above described methods may be used for checking the working power of the standard uranium, and if proper care be used, the results will be found to agree very closely.

5. Estimation of Phosphoric Acid in Minerals or other substanc containing Iron or Alumina.

In order to make use of any volumetric process for this purpo the phosphoric acid must be separated. It is true there a methods in vogue which profess to accomplish the object in t presence of these substances, but they cannot lay claim to accurac and are not worth consideration.

There are five methods of separation available :—

α. By molybdic acid, (applicable to all minerals, soils, an manurial substances.)

β. By digestion with 5% sulphuric acid solution, (applicabl to raw phosphates containing a moderate quantity of iron o alumina, or both, such as Lahn phosphates, coprolites, &c.)

γ. By Reynoso and Girard's method as stannic phos phate, (applicable to the same.)

δ. By Chancel's bismuth process, (applicable to the same,) i the absence of sulphates and chlorides.

ε. By Joulie's ammonio-magnesic citrate process, (applicable to the same,) and to manures in general.

Another admirable method of separating phosphoric acid from iron and alumina is described by Flight, (Chem. Soc. Journ, ser. 2, vol. xiii, p. 592,) but as this is adapted more to minerals containing phosphoric acid mainly in combination with iron and alumina, it need not further be described here.

a. Separation by Molybdic Solution.

Molybdic solution is best prepared by dissolving 150 gm. of ammonic molybdate in 1 litre of water, and pouring it into 1 litre of commercially pure nitric acid of sp. gr. 1·20 or thereabout, (the mixture must not be reversed.) About 100 c.c. of this solution suffices to precipitate 0·1 gm. of phosphoric acid, and it is not advisable to take a much greater quantity for separation. The mineral is best brought into solution by nitric acid; sulphuric acid may be used, but in cases where lime is the base, it is obviously inadmissible; hydrochloric acid or chlorides must not be present in any large quantity, nor arsenic, silicic, or organic acids.

The somewhat concentrated clear solution of the substance being prepared, molybdic solution is added in the proportion mentioned, and the mixture allowed to stand at a temperature of about 50° C for five hours, (special experiments have proved conclusively that this is sufficient,) it is then cooled, the yellow precipitate brought upon a small filter, and washed with a mixture of molybdic solution and water in equal proportions; if the washing is carefully done, it will not require more than double the volume of the original liquid.

The precipitate is then dissolved in the least possible quantity of warm diluted ammonia, (1 part of strong liquid ammonia and 3 parts of water,) and the excess of ammonia nearly neutralized with hydrochloric acid; the liquid is then cooled, and the phosphoric acid precipitated with 'magnesia mixture' in the proportion of about 10 c.c. to 0·1 gm. of P^2O^5.

The 'magnesia mixture' is best made by dissolving 110 gm. of magnesic chloride and 140 gm. of ammonic chloride in 1300 c.c. of water, and diluting the mixture to 2 litres with strong liquid ammonia; 10 c.c. of this clear mixture is nearly twice as much as is necessary to precipitate 0·1 gm. P^2O^5, but the excess is advisable, since it prevents the solubility of the double phosphate. After adding the precipitant, strong ammonia is poured into the mixture to about one-third of the volume—the total volume for 0·1 gm. P^2O^5 should be about 100 or 120 c.c. After standing three to four hours, (special experiments have proved this to be quite sufficient,) the precipitate is collected on a small filter, washed moderately with ammoniacal water, then dissolved with a few drops of strong hydrochloric acid and hot water, the filter washed with repeated small portions of hot water, the excess of acid cautiously neutralized with dilute soda or potass, so that a faint precipitate is formed—then 5 c.c. of sodic acetate solution (§ 69.2 *c.*) added, which should again render the liquid clear, and the solution titrated with standard uranic acetate as before described.

The usual course adopted when the molybdic method of separation is employed, is to ignite and weigh the precipitate as magnesic pyrophosphate, (see p. 223,) and this is undoubtedly the most correct way, but nevertheless it is possible to obtain very good results volumetrically. In either case the separation and estimation are tedious, troublesome, and somewhat costly, but I have given the latest approved methods of conducting the operations, and they certainly have the merit of being extremely accurate.

β. Extraction of the Phosphoric Acid mainly as Calcic Phosphate by dilute Sulphuric Acid, (Graham's Method.)

10 gm. of the very finely powdered phosphate are weighed in a platinum or porcelain crucible, or in a small sheet-iron pan, and placed over a gas or spirit lamp for about ten minutes, keeping it at a dull red heat; then set aside to cool; when cold transferred to a mortar, and rubbed down to a fine powder, adding gradually 200 c.c. of cold dilute sulphuric acid, containing 5 per cent. of H^2SO^4.

The mixed acid and phosphate are transferred to a litre flask, the mortar repeatedly rinsed out, first with portions of the measured acid, and lastly with water, till the measure is made up; the whole is then well shaken occasionally, and after three hours set aside to deposit, or, if necessary, at the end of three hours a portion may be filtered for the analysis, which is conducted as follows:—

100 c.c. of the clear fluid from the flask are measured into a beaker, 10 drops of a saturated solution of citric acid added, then cautiously neutralized with potash or soda, acetic acid is then added in excess; then 10 c.c. of the sodic acetate solution, (§ 69. 2. *c*.) and the titration with uranium completed in the usual way.

The separation of the iron and alumina by this method is not absolutely complete, and it is of course necessary that there should be sufficient lime present in the original material to combine with the phosphoric acid. Traces of iron will generally be found to occur in the sulphuric acid solution, nevertheless, for approximate purposes, such as samples of raw phosphates for manure manufacturers, it gives very fair results.

γ. Separation by Tin (Reynoso and Girard).

To the solution of the substance in nitric acid pure granulated metallic tin is added, in the proportion of five or six parts to every part of phosphoric acid supposed to be present, and the mixture digested on the water bath for two or three hours; the fluid is then carefully decanted off through a filter, and repeatedly washed y decantation with hot water; yellow ammonic sulphide is then dded to the precipitate in the beaker to dissolve all the stannic hosphate, and whatever traces may have been retained on the lter are removed by eventually passing the sulphide solution hrough it; the insoluble compounds of alumina and iron are thus tained on the original filter, and washed with water containing mmonic sulphide. Magnesia solution is then added to the clear reenish-yellow filtrate and washings, to precipitate all the phoshoric acid as double phosphate of magnesia and ammonia, which collected, washed with ammoniacal water, dissolved in acetic acid, nd titrated with uranium as before described.

δ. Separation by Bismuth (Chancel).

This process has given exceedingly good results in separating osphoric acid from iron and alumina, but unfortunately is not ailable in the presence of chlorides or sulphates. It has been pecially used in the estimation of P^2O^5 in the German phosates, phosphorite, native phosphate of alumina, &c.; and in mparison with the molybdic and magnesia processes by weight, s given fairly accurate results in a very much shorter time. ee Birnbaum Zeitschrift für an Chem., vol. ix. p. 203.)

The procedure is as follows:—2 gm. of the very finely powdered ineral are covered with 6-7 c.c. pure nitric acid of sp. gr. 1·25, and pt at about 90° C. for twenty minutes, then diluted with water d filtered. The filtrate is diluted to 500 c.c., sufficient for five parate estimations if required, 100 c.c. only being taken, equal 0·4 gm. mineral. The 100 c.c. are diluted with the same lume of water, the fluid then brought to boiling, and precipitated th a solution of bismuthic nitrate prepared in the following nner:—Crystals of bismuthic nitrate are treated with water and t so much nitric acid added that on further dilution with water milkiness takes place, the proportion of bismuth should be ut 25 gm. per litre; sufficient of this solution being added to nbine with all the P^2O^5, the vessel is set aside to cool, by which ans the precipitate becomes crystalline, and moreover, the whole the bismuthic phosphate will be separated from the fluid, which uld not be the case in the hot liquid. The fluid is decanted ough a filter, adding cold water repeatedly to the main preitate in the beaker, and pouring off; when sufficiently washed, filtrate is treated with a few drops of hydrochloric acid to solve the small quantity of precipitate upon it, washed, and the d so obtained mixed with the main precipitate. Ammonia, and monic sulphide are then added in tolerable quantity, and the ture digested till the precipitate is quite black; acetic acid in ess is then added, and the mixture heated nearly to boiling for a short time, filtered when settled clear, washed, the remaining traces of H^2S in the fluid removed by a little chlorine water, and then titrated with uranium solution as usual.

The titration with uranium must be adopted, since the bismuthic precipitate is not of constant composition; however, it contains all the P^2O^5 in the original compound, and can be recovered as ammonic phosphate, the bismuth being all removed as sulphide. It is absolutely necessary that no hydrochloric or sulphuric acid is present in the original solution in which the precipitation takes place.

ε. Citric Acid Method (Joulie).

This process has derived some notoriety from the fact that it is recommended as the best for the analysis of phosphatic materials by a commission on Manures,* appointed by the French Agricultural Society.

It is in many respects similar to the method adopted by Fresenius, Neubauer, and Luck, (see § 75,) and consists essentially in precipitating the phosphoric acid from its combinations with calcium, iron, and alumina, as double phosphate of magnesia and ammonia in the presence of ammonic citrate, and the subsequent titration of the precipitate with uranium solution. Of course it is a matter of no consequence whether the precipitate so obtained is contaminated with calcium, so long as the whole of the phosphoric acid is carried down, free from iron and alumina, and in such a form as to be readily titrated by uranium. The description of the process has only come under my notice ‡ while this section is being printed, and consequently I have had no time to examine it thoroughly. The experiments made by me, however, have given very promising results.

Joulie has adopted a systematic method in which all classes of manures containing phosphates are treated alike, whether iron or alumina are, or are not, present. This insures uniformity in titration, since approximate quantities of re-agents are used in all cases.

In the case of raw phosphates, 5 gm. of material are dissolved in hydrochloric acid, if necessary, with the addition of nitric acid, the solution filtered and diluted to a definite measure, say 200 or 250 c.c.

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*Bulletin de la Société des Agriculteurs de France, 1876, p. 53, et suivantes.

‡ Methode Citro-uranique pour le Dosage de l'Acide Phosphorique dans les Phosphates et les Engrais—par M. H. Joulie, Annuaire de la Pharmacie, 1875, Rédigé par Dr. C. Méhu.

The quantity recommended for titration is such that it shall contain from 20 to 40 milligrammes of phosphoric acid; a trial may first be made with 10 c.c. of the dissolved material and the amount of precipitate obtained by the magnesia mixture will indicate to an expert somewhere about the proportion of phosphoric acid present, and serve as a guide to the quantity of liquid to operate upon.

The citrate of magnesia solution used for precipitating the phosphoric acid is prepared by dissolving 400 gm. of citric acid in 200 gm. of warm water, adding 22 gm. of pure magnesic carbonate, and when all effervescence is over and the liquid clear, pouring into the mixture 400 c.c. of solution of ammonia of sp. gr. 0·920; lastly the whole is diluted to the measure of 1 litre; it should be strongly acid.

10 c.c. of this solution amply suffices to precipitate 40 mgm. of phosphoric acid; and the operation is best made in a small flask, gently shaking the mixed cold liquids, adding ammonia freely in excess, and setting quietly aside for two hours in order that the crystalline precipitate may separate. Two hours have been proved sufficient under all varying circumstances.

The precipitate is then filtered on a small filter (very porous paper may be used) and repeatedly washed with small quantities of ammoniacal water. The precipitate is then dissolved on the filter with 10 c.c. of nitric acid (1 : 10); first, washing out the precipitating flask with it to dissolve traces of crystals which may adhere, finally washing the filter with repeated small quantities of boiling water, and receiving the filtrate into a beaker capable of holding about 150 c.c. and marked at 75 c.c. A small filter about one inch in depth is quite large enough for the purpose, and permits of being well washed without the use of large volumes of liquid; when the precipitate is dissolved and the filter properly washed, the total amount of liquid need not exceed 30 c.c.; to this clear solution dilute ammonia is cautiously added drop by drop, until a persistent cloud is produced, 5 c.c. of solution of sodic acetate is then added, the mixture heated on the water bath to 90° or 100° C and the titration completed as described on page 230.

Joulie prefers to standardize his solution of uranic nitrate by means of a weighed quantity of pure ammonic phosphate. 3·087 gm. of this salt previously dried at 100° C are dissolved in a litre of water, the solution so obtained contains 2 gm. of phosphoric acid, and consequently 20 c.c. represents 40 milligrammes.

An approximate uranium solution is obtained by dissolving about 40 gm. of uranic nitrate in a litre of water and adding to it ammonia till a persistent precipitate occurs, then free acetic acid in slight excess, and filtering after a day or two to remove any basic salt or traces of uranic phosphate which may be present.

Titration of the Uranium Solution. 20 c.c. of the standard ammonic phosphate and 5 c.c. of sodic acetate are measured into a beaker, holding about 150 c.c. and marked at 75 c.c., then diluted to 75 c.c. and heated to near boiling; the uranium solution is then cautiously delivered into the mixture until a test taken in the usual way with ferrocyanide shows the brown colour.

Joulie makes a correction for the excess of uranium necessary to give this colour, but as all the titrations are supposed to take place under the same conditions as to volume of liquid and quantities of re-agents, it is not a matter of great importance.

The Analytical process: The working power of the uranium solution having been proved by the titration just described and which is of course repeatedly done till the exact point is ascertained, the operator is in a position to titrate any given specimen of phosphate. To resume therefore the operation of preparing the raw material and obtaining the precipitate from the citro-magnesic solution, a volume of the phosphate solution corresponding to 30 or 40 mgm. of phosphoric acid or as near thereto as is possible is precipitated, the precipitate dissolved, 5 c.c. of sodic acetate added, diluted to 75 c.c., then heated to boiling, and the approximate amount of uranium ascertained; a second trial is then made, adding at once before heating nearly the necessary quantity of uranium, and finally drop by drop till the exact point is known—thus, to give one of Joulie's examples, suppose 5 gm. of material has been weighed and dissolved in 20 c.c. of nitric or hydrochloric acid and the solution made up to 100 c.c. 20 c.c. of this solution representing 1 gm. of material is precipitated as described, and requires 16·2 c.c. of uranium, of which each c.c. = 0·00476 gm. P^2O^5, then 16·2 × 0·00476 = 0·077112 gm. or 15·42% P^2O^5.

The quantities operated upon by Joulie are very small and liable in the hands of careless operators to give rise to serious errors; nevertheless, experiments made by myself upon phosphates containing iron and alumina as well as pure calcic phosphates have given very concordant results, the precipitates being entirely free from both iron and alumina.

The chief value of the process is the method of separating the phosphoric acid in such a clean form as to be available for titration. Other portions of Joulie's method relating to reduced and assimilable phosphates and their estimation by means of alkaline ammonic citrate or oxalate are of questionable value and hence are not given here.

SUPERPHOSPHATES.

robably there exists no substance which admits of more epancy in analytical results than the so called superphosphate ime. It is evident that this discrepancy is mainly due to the us methods of extraction of the soluble phosphoric acid ted by different analysts.

aw phosphatic materials consisting mainly of insoluble tricalcic phate ($Ca^3P^2O^8$) when treated with sulphuric acid by the ufacturer give rise to the production of soluble mono-calcic phate ($CaH^4P^2O^8$), together with calcic sulphate and small tities of magnesia, iron, alumina, organic matter, &c.

long series of experiments have proved that the soluble phoric acid existing in such a mixture is immediately removed old water.

would tend very much to uniformity of results among ysts if the method of extraction adopted by the Magdeburg ciation of Agricultural Chemists were in general use, and h simply consists in weighing 20 gm. of the sample, ferring to a mortar, adding cold water, and gently breaking n any lumps with the pestle without grinding the residue, and ith repeated small quantities of water transferring the whole litre flask; the exact measure is then made up with water, ixture vigorously shaken, and the required portion immediately ed through a dry filter for titration with uranium, or for sis by any other chosen method.

c.c. of the solution so prepared represents 1 gm. of super- hate, and with ordinary manufactures this is a convenient tity for titration. In the case of very rich preparations such solved guanos or concentrated manures, 10 gm. should be ed instead of 20 gm., or if 20 be used, 25 c.c. only of the ion with 25 c.c. of water should be taken instead of 50 c.c. tration.

Uranium Solution. For the analysis of manures it is dingly convenient to have this solution of such strength that c.c. represents one per cent. of tribasic calcic phosphate red soluble by acid, when 1 gm. of the manure is taken for sis.

is strength is a convenient one also for the uranium solution, very nearly the same as described on pp. 220, 1, 2. Acetate is to be preferred to nitrate on some accounts, neverthe salt will answer the purpose.

The solution must be standardized by pure tricalcic ph described on page 223, taking great care that the salt i immediately it has cooled after ignition, so as to have no moisture; it is of course impossible to weigh any exact q this substance, but if rather more than 5 gm. of t precipitated calcic phosphate be taken, well moistened strong nitric acid and warmed, then dissolved complet addition of water and finally diluted to 500 c.c., a soluti obtained which can at any time be used for the accurat of the uranium solution. It is only necessary to evapor of it to dryness, moistening with excess of strong amm igniting and weighing the residue of pure tribasic calcic p from this may be calculated the exact amount of materi c.c. Supposing it to be slightly above 5 gm. sufficient be added to the solution so that 1 gm. exactly shall be in 100 c.c.; a standard solution is thus formed which ca for titrating the uranium and needs no calculation.

25 or 30 c.c. of this solution representing a 25 or 3 phosphate are convenient quantities to take for the titrat uranium solution, but it is advisable always to use about volume of liquid, and hence water must be added to ma measure to about 50 c.c.; the standard solution being necessary to neutralize cautiously with soda or potash till persistent precipitate occurs, then to add 10 c.c. of so solution, the free acid in which will re-dissolve the cloud about 20 c.c. of uranium are ran in and the mixture near boiling, and the titration finished as before describe

Superphosphates containing Ammonia.

Where ammoniacal salts are present in superphosphat phosphatic manures, the uranium solution which standardized, merely on calcic or sodic phosphate, represent accurately the amount of phosphoric acid; colour with ferrocyanide occurs sooner in the titration t ammonia is absent, and this is more particularly the uranic nitrate, it is difficult to account for this but it hence with superphosphates containing salts of ammo genous organic matter has not the same effect,) the work of the uranium solution should be taken on the standard calcic phosphate with 2 or 3 c.c. of a saturated solution of ammonic acetate, chloride, or sulphate added.

Superphosphates containing Iron and Alumina.

The presence of these bodies may be known immediately by a semi-transparent gelatinous precipitate being produced in the clear solution of manure, when 10 c.c. of acid sodic acetate is added to the 50 c.c. of phosphate solution. If there are only faint traces of ferric phosphate, which is generally the case in superphosphates, it may be disregarded, but if more than this occurs the precipitate must either be weighed as such and the clear calcic solution titrated by itself or Joulie's method of separation may be adopted, (see page 229,) or again, ammonic citrate and acetate may be added to the solution instead of sodic acetate to prevent the precipitation of iron and alumina, in which case, however, the working power of the uranium must be known in the presence of similar quantities of these salts by a blank titration with calcic phosphate.

If it be desired to weigh the precipitate of iron and alumina phosphates, 200 c.c. of the manure solution should be mixed with 50 c.c. of the usual acid sodic acetate solution and the resulting precipitate filtered off, washing it on the filter three or four times with small quantities of boiling water, (too much water must not be used as it is not perfectly insoluble,) then ignited and weighed; calculating 47 per cent. of it as phosphoric acid.

50 c.c. of the filtrate kept separate from the washings = 40 c.c. of the original solution may then be titrated with uranium as usual.

In cases where very large quantities of iron are present the extraction of the soluble phosphoric acid should be accomplished with the least possible quantity of water, since the addition of much water rapidly decomposes the ferric phosphate from the soluble to the insoluble form, and hence the filter pump is of great service in such a case, but as such a material is not available for any process of titration it need not be further alluded to here.

TANNIC ACID.

§ 70. THE estimation of tannin in the various astringent materials used in tanning by volumetric methods is not of the most satisfactory character. A great variety have been proposed, for the miscellaneous substances used in tanning, the best of which appears to be the gelatine process, as modified by Mulder, Löwenthal's process modified by Neubauer for oak-barks and similar substances, and Fletcher's lead method for tea, or other substances containing gallo-tannic acid.

Extraction of the Tannin from Barks, Leaves, &c. The best method is first to reduce the material to coarse powder and to exhaust 20 gm. of it by digestion with cold water, using a strong press if possible, the residue is then boiled for half or three-quarters of an hour, replacing the evaporated water; the liquids are then mixed together and diluted to 1 litre. A further quantity of astringent matter can be removed from the residue if boiled with acidulated water, but as this method is not used in the actual tanning process it is not available for the tanner, and consequently need not be done in testing.

Watts (Pharm. Journ., March 1867), who has had considerable experience in the valuation of tanning materials, thus describes the gelatine process alluded to:—

1. By Standard Gelatine Solution.

Dissolve in a litre of water 3 gm. of isinglass, and add to it about 1 gm. of powdered alum. To ascertain the quantity of tannin which 1 c.c. of this solution represents, dissolve 2 gm. of pure tannic acid in 1 litre of water for a standard solution, of which every 10 c.c. will therefore contain 0·02 gm. of tannic acid. Measure 50 c.c. of this latter solution, containing 0·1 gm. of tannic acid, into a beaker; dilute it somewhat with water, and drop in from a burette the gelatine solution until the falling of a drop on the surface no longer produces the characteristic ring of tannate of gelatine, then allow the precipitate to settle; next take a drop out carefully by the end of a glass rod, drop it on to the surface of a black glass plate, and there test it for excess of either tannin or gelatine, by bringing in contact with it a drop of either solution, observing whether any cloudiness occur at the junction of the two drops; when the exact point has been ascertained at which the gelatine no longer produces a precipitate, which requires some practice to hit exactly, the number of cubic centimetres of gelatine solution consumed correspond to 0·1 gm. of tannic acid.

2. Löwenthal's process modified by Neubauer.

The requisites for this method are:—

(1.) **A Solution of Sulphindylate of Potassium** (indigo-carmine) 30 gm. to the litre. This solution is to be carefully heated in-closed bottles to 70°, whereby its tendency to form confervoïd growths is checked. Only the purest indigo-carmine can be used. 20 c.c. of the solution are diluted to ¾ litre, and after the addition of 10 c.c. of dilute sulphuric acid, titrated with potassium permanganate; the colour must change ultimately from greenish to a clear golden yellow, and this change must take place with precision, otherwise the solution is useless.

(2.) **Tannin Solution.** Chemically pure tannin is dried at 100°, and 2 gm. are dissolved in 1000 c.c. There is little doubt that the differences between chemists in their analyses of oak-bark are probably due in many cases to their having operated with standard solutions of tannin of different degrees of purity. For testing the purity of commercial tannin Neubauer recommends Hammer's process, viz., the observation of specific gravity before and after the tannin has been absorbed and removed from solution by rasped hide.

(3.) **Solution of Potassium Permanganate** containing 1·666 gm. of pure crystallized potassic permanganate in 1 litre of water.

(4.) **Decinormal Solution of Oxalic Acid** may be used for titration of the permanganate, instead of the tannin solution. This would contain 6·3 gm. to the litre, and according to the author's experiments will correspond to a tannin solution containing 4·157 gm. of tannin per litre.

(5.) **Pure Animal Charcoal** exhausted with hydrochloric acid, and well washed until the chlorine reaction disappears; it is preserved under water.

(6.) **Pure Dilute Sulphuric Acid.** (1 to 5).

The Analytical process. To 20 c.c. of the indigo solution diluted with ¾ litre of water are added 10 c.c. of the sulphuric acid, and then the permanganate solution is slowly run in, the liquid being constantly and vigorously stirred; the blue colour passes through various shades of green, turning to a slightly greenish-yellow, and ultimately a bright golden yellow; this change of colour is the terminal point of the reaction, and as it is not easy to see the pink colour of the permanganate in the yellow solution, the disappearance of the green must be carefully noted. The operation is now to be repeated with a fresh portion of the indigo solution and 10 c.c. of the tannin solution, the difference between the amounts of permanganate used is the measure of the tannin. 20 c.c. of the indigo solution should always require at least as much permanganate as 10 c.c. of the tannin solution; it is better that they should require half as much again.

Titration of an Oak-bark extract. This is performed as above described. If one litre of extract has been prepared from 20 gm.

of oak-bark powder, from 10 to 20 c.c., according to the quantity of tannin present, are employed in the titration. Repetitions of the analysis give closely concordant results. The tannin used in titration being obtained from the gall-nut is not identical with that contained in the oak-bark. Again, oak-bark tannin is not a pure substance; but though the extract of the oak bark contains many other matters besides tannin which reduce permanganate, still the action of most of these matters is slow, and their effect consequently small.

Neubauer takes three equal portions of the extract, one is titrated as above; to the two others equal quantities of animal charcoal are added. After standing for a few moments a sample from one of them is filtered and tested by adding to it, first sodic acetate, and then ferric chloride. If no dark brown precipitate due to tannin can be detected, the other portion which has been treated with animal charcoal is filtered, the charcoal washed, and the filtrate treated as before. The amount of permanganate required by this is subtracted from that required by the portion of the extract not treated with animal charcoal. The difference is the measure of the tannin. The author points out that there may be matters present which would reduce permanganate and be at the same time precipitable by charcoal; were gallic acid present, it would belong to this category, but it is doubtful if there is anything more than a trace of this substance in oak-bark.

3. By Standard Lead Solution (Fletcher).

In the case of tea, Allen has pointed out that the astringency is probably due to a mixture of tannic and gallic acids (Chem. News, xxix, 169). The lead process estimates these together and for all technical purposes it suffices to consider them as tannin.

The Analytical process. 5 gm. of lead acetate are dissolved in water and diluted to 1 litre, and the solution filtered after standing. The indicator is made by dissolving 5 milligrammes of pure potassic ferricyanide in 5 c.c. of water, and adding an equal bulk of strong ammonia solution. One drop of this test will detect 0·001 milligramme of tannin, or 1 milligramme dissolved in 100 c.c. of water.

The precipitating power of the lead solution is ascertained by diluting 10 c.c. of it to about 100 c.c. with boiling water, and adding to it, from a burette, a solution of 0·1 gm. of pure tannin in 100 c.c. of water. After adding 10 c.c. of the latter solution, about 1 c.c. of the liquid is withdrawn with a pipette and passed through a small filter, the drops being allowed to fall on to spots of the indicating solution previously placed on a porcelain slab. If no pink colouration is observed, another small addition of the tannin solution is made, a small portion of the liquid filtered, and added to the indicator as before, the process being repeated until a pink colour is observed. The greatest delicacy is obtained when the drops of liquid from the funnel are allowed to fall directly on to the spots of the indicator, instead of observing the point of junction of the liquids.

The reaction being complete, a second estimation is made, and in this case almost the full volume of tannin solution can be added at once.

It is necessary to use the purest tannin for the purpose, as a serious error may otherwise occur, some samples of commercial tannin having little more than half the precipitating power of the best.

Exactly the same process is employed for estimating the tannin in tea, the decoction being substituted for the standard tannin solution and added to the lead solution as before.

The solution of tea is prepared by boiling 2 gm. of the finely-powdered sample with about 80 c.c. of water for half an hour. The decoction is strained through fine muslin, the particles of leaf returned to the flask, and the boiling resumed for an hour with the same quantity of water as before. The process is repeated till no more colouring matter is extracted. The whole of the solution is set aside, to allow any particles that may have passed through the muslin to subside, when the liquid is decanted from the sediment, the last portions passed through a filter, and the whole decoction made up to 250 c.c. This diluted solution is ready for use in the burette, the remainder of the process only occupying a few minutes.

The volume of tannin, or tea solution, it is necessary to add to 100 c.c. of pure water, in order that a drop may give the pink reaction with the ferricyanide, is substracted from the total amount run from the burette.

If the solutions are made of the strength here described, 10 c.c. of the lead solution will precipitate about 10 milligrammes of pure gallotannic acid, and therefore the volume of tea solution added contains 0·01 gm. of tannin.

If all the weights and volumes above mentioned are observed, 125, divided by the number of c.c. of tea solution used, will give the percentage of tannin, &c., in the sample.

It has been ascertained that prolonged boiling does not affect the precipitating power of the tea, and solutions of the same sample prepared on different occasions have given absolutely concordant or closely agreeing results. The percentage of tannin in tea can be ascertained by this process to within 0·2 per cent.

SUGAR.

§ 71. The term sugar is applied to several bodies possessing distinct properties, and differing somewhat in chemical composition.

There are only two classes, however, of general importance, to say:—

1. Those that possess the chemical composition of grape su glucose, $C^6H^{12}O^6$, such as the sugar contained in the juice of apples, and other ripe fruit; also that which occurs in u *Diabetes mellitus.*

2. Common cane sugar, $C^{12}H^{22}O^{11}$, contained in the juice sugar cane, beet root, maple, &c.

Sugars of the latter class, and also those contained in may all be converted into grape sugar by boiling for minutes with weak sulphuric or hydrochloric acid, and must so converted before they can be estimated by the chemical m here given.

This inverted sugar is not identically the same as grape su has however the same effect upon the copper or mercury so which is all that is required for analytical purposes.

1. By Standard Copper Solution (Fehling).

This method is based on the fact, that although a mix pure cupric sulphate, potassic tartrate, and caustic soda, mi proper proportions, may be boiled without undergoing chang if only a trace of grape sugar be added, a very slight warn enough to precipitate a portion of the copper as protoxide, C

Fehling, Neubauer, and others, have very carefully exa the reaction which takes place, and found that 1 eq. pure sugar=180, is capable of reducing exactly 5 eq.=397 of oxide (CuO) to the state of cuprous oxide (Cu^2O). There the quantity of copper reduced by a given solution of su known, it is easy to find the quantity of sugar present.

There are three methods of procedure—

(1.) To prepare a standard solution of pure cupric sulphat potassic tartrate and caustic soda, and add the sugar solutic definite quantity of it until the deep blue colour has disapp or—

(2.) To add the copper solution, which may be of ind strength, in excess, and estimate the precipitated protoxide, by weight or indirectly, by the method of Schwarz, § 44.2.

(3.) To add the standard solution of copper in excess measured volume of the sugar solution and boil so as to prec the cuprous oxide; the blue supernatant solution is then f away and the copper estimated by stannous chloride as described in Weil's process, § 44. 7.

As the first method is susceptible of very accurate results, and occupies little time, it is generally preferred. The requirements are as follows:—

Standard Solution of Copper. 34·64 gm. of pure crystallized cupric sulphate, previously powdered and pressed between blotting paper, are weighed and dissolved in 200 c.c. of distilled water; in another vessel, 173 gm. of pure crystals of Rochelle salt are dissolved in 480 c.c. of solution of pure caustic soda, sp. gr. 1·14. The two solutions are then mixed, and the deep clear blue solution diluted with distilled water to 1 litre.

Löwe advocates the use of glycerine instead of alkaline tartrate in making this solution (Zeitschrift für an Chem., ix. p. 20), using about 20 gm. of glycerine for the amount of copper above described. The solution so made, however, will not bear much diluting without becoming turbid, and as glycerine is frequently contaminated with sugar as an adulteration, the modification does not seem to possess any advantage over the original method.

Each 10 c.c. of the solution so prepared, containing 0·3464 gm. of cupric sulphate, represent exactly 0·050 gm. of pure anhydrous grape sugar. It must be preserved in a dark place, and in well-stoppered small bottles, kept tolerably full, since, if the solution absorbs much carbonic acid, a precipitate will occur in boiling even in the absence of sugar. This may, however, be prevented by adding fresh caustic alkali. In all cases, before using it for titrating a solution of sugar, 10 c.c. should be boiled with about 40 c.c. of water, for a few minutes, in order to be certain of its fitness.

The Solution of Sugar. This must be so diluted as to contain ½ or at most 1 per cent. of sugar; if on trial it is found to be stronger than this, it must be further diluted with a measured quantity of distilled water.

If the sugar solution to be examined is of dark colour, or likely to contain extractive matters which might interfere with the distinct ending of the reaction, it is advisable to heat a measured quantity to boiling, and add a few drops of milk of lime, allow the precipitate to settle, then filter through animal charcoal, and dilute with the washings to a definite volume.

From thick mucilaginous liquids, or those which contain a large proportion of albuminous or extractive matters, the sugar is best extracted by Graham's dialyser.

The method may be applied directly to diabetic urine (see Analysis of Urine), as also to brewer's wort or distiller's mash. Dextrine does not interfere, except the boiling of the liquid under titration is long continued.

Cane, beet, and maple sugar juice, or prepared sugars, are converted into grape sugar by heating 30 or 40 c.c. of the clarified liquid in a water bath, with 30 or 40 drops of dilute sulphuric or hydrochloric acid (1 to 5), for twenty minutes, replacing the evaporated water from time to time, so as not to char the sugar; the acid is then neutralized with sodic or calcic carbonate, and the liquid diluted to 15 or 20 times its volume before being titrated.

100 parts of grape sugar so found represent 95 parts of cane or beet sugar, or 10 c.c. of copper solution are reduced by 0·0475 gm. of cane or beet sugar. Starch or dextrine, or substances containing them, require to be heated longer with the acid in order to insure their conversion into glucose. To convert 1 gm. of starch into dextrine, and thence into sugar, it should be mixed with 30 c.c. of cold water, smoothly, then heated gently until thick, then add 30 drops of dilute acid, and boil in a small flask, supported obliquely on a sand bath for 8 or 10 hours, replacing the water from time to time; then neutralize and dilute as before.

The change may be produced more rapidly and at lower temperature by using some form of diastase in place of sulphuric acid; an infusion of malt is best suited to the purpose, but the temperature must not exceed 71° C. (160° Fahr.): about four hours' digestion is sufficient. A like quantity of the same malt solution must be digested alone, at the same temperature, and titrated for its amount of sugar, which is deducted from the total quantity found in the mixture. O'Sullivan (Journ. Chem. Soc., 1872, p. 579), has, however, clearly shown that the effect of the so-called diastase is to produce a body called maltose, which has only the power of reducing the copper solution to the extent of about two-thirds that of dextrose or true grape sugar, the rest being probably dextrine; sulphuric or other similar acids cause complete inversion.

100 parts of grape sugar so found represent 90 parts of starch or dextrine $(C^6H^{10}O^5)n$, or 10 c.c. copper solution, are reduced by 0·45 gm. starch or dextrine. When dextrine is present with grape sugar, care must be taken not to boil the mixture too long with the alkaline copper solution, as it has been found that a small portion of the copper is precipitated by the dextrine (Rumpf and Heinzerling Zeitschrift für an Chem., ix. 358).

Sugar of milk $(C^{12}H^{22}O^{11})$ may also be converted into grape sugar by boiling for a short time with dilute sulphuric acid, before being estimated.

The Analytical process: 10 c.c. of the copper solution are measured into a convenient sized flask or a white porcelain dish, and diluted with 40 c.c. of water, or if necessary, the same quantity of dilute caustic soda, and brought to gentle boiling. The dilute sugar solution is then delivered in from time to time from a graduated burette; when the precipitated oxide appears of a bright red colour, the lamp should be removed and the precipitate allowed to settle; if the flask is then held before a window, or the dish lifted on one side so as to cause the clear liquid to flow against the white porcelain, the colour may readily be seen; should any blue tinge remain, more sugar solution is added, and the boiling recommenced and continued until all colour just disappears. If any doubt exists, a small portion of the *hot* mixture should be filtered, acidified with acetic acid, and a drop of solution of potassic ferrocyanide added; if copper is in excess, a brown colour or precipitate will be produced.

It is almost impossible to hit the exact point on the first trial, but it affords a very good guide for a more exact titration the second time; the quantity of sugar solution necessary to discharge the colour from 10 c.c. copper solution contains 0·05 gm. of grape sugar.

When the titration is once commenced it should be carried on s quickly as possible in order to prevent irregularities from long xposure of the hot solution to the atmosphere.

2. By Mercuric Cyanide (Knapp).

The principle of this method is based on the fact that if a lution of grape sugar be added to a boiling solution of mercuric anide rendered alkaline by soda or potash, the mercury salt is duced to metallic mercury in the proportion of 100 parts of hydrous grape sugar to 400 parts of mercuric cyanide.

The standard mercury solution is made by dissolving 10 gm. mercuric cyanide in about 600 c.c. of water then adding 100 c.c. caustic soda solution of sp. gr. 1·145 and diluting to 1 litre. This solution possesses the advantage over **Fehling's** that it ll keep a long time without deterioration.

The Analytical process. 40 c.c. of the mercury solution is ced in a small flask, heated to boiling, and the ½ per cent. sugar ution allowed to run in with continued heating until the whole the mercury is precipitated; the volume of sugar solution so d contains 100 milligrammes of grape sugar.

The ending of the process is ascertained by bringing a drop of e supernatant liquid into contact with filter paper tied over a all beaker containing strong solution of ammonic sulphide. hen a brown colour ceases to form with the vapour of the phide all the mercury is precipitated. Sharper results may be tained by moistening pure filter paper with the supernatant uid, and holding quite close to it, for half a minute, a glass l dipped in the sulphide solution. While the mercury is in excess a decided brown colouration takes place, but towards the end of the reduction it becomes fainter and fainter until only a slight ring of pale colour occurs. If the paper is allowed to dry a stronger colour will result, since a trace of undecomposed cyanide is invariably present, hence the fresh moist effect must always be taken as the final point.

To be certain of the total decomposition of the cyanide a few c.c. may be filtered, acidified with acetic acid, and tested with sulphuretted hydrogen water for mercury.

Special experiments have shown that the estimation of sugar by this process agrees closely with the results obtained by Fehling's solution.

INDIGO.

§ 72. This substance, as met with commercially, is of very variable composition, and a great many processes have been from time to time proposed for estimating the amount of pure indigotin or blue matter present. These processes have for the most part been based upon experiments made with the pure material, and their accuracy has totally disappeared when used upon material containing other vegetable or earthy matters, such as are constantly to be found in marketable indigo.

These impurities are mainly indigo-gluten, indigo-brown, indigo-red, and ferric oxide, which latter would be found of course in the ash.

The volumetric processes here given are such as have been found to give the most reliable results, and may be depended upon for technical purposes. In both processes the sample is to be dissolved in fuming sulphuric acid previous to being titrated.

This is best done as follows:—1 gm. or 10 grn. respectively of the very finely powdered indigo is put into a closely stoppered small flask, or bottle, with 8 gm. or 80 grn. of acid (the relation being in each case 1 to 8), together with about a teaspoonful of small garnets, or if these are not at hand, flint pebbles or broken hard glass, the flask closely stoppered and kept for 8 or 10 hours in a warm place not exceeding 50° C. with frequent shaking; the sample is then ready for examination by either of the following processes:—

1. By Potassic Bichromate (M'Kinlay).

10 grns. of the indigo dissolved as described above are placed in a white porcelain basin capable of holding about two pints, and

liluted with one pint of water, the bottle being repeatedly washed ut with water so as to remove all colour from the garnets or glass. 50-60 grs. of oxalic acid are then added, previously dissolved in a ew ounces of water; the whole may now be diluted to about 30 luid ounces, and is ready for titration.

Standard Potassic Bichromate, containing 60 grs. of bichromate n 1000 dm. of water, each dm. of this solution equals 1 per cent. f pure indigotin.

The same solution can of course be made on the gramme system y dissolving 6 gm. of bichromate in 1 litre of water, so that when gm. of indigo is taken for analysis, 1 c.c. of bichromate will also qual 1 per cent. of pure indigo blue.

The titration is now performed by running the bichromate into e slightly warm indigo mixture with frequent stirring until no ue or green colour can be seen on placing a drop of the mixture white filtering paper.

In adding the bichromate solution to the blue liquor, and parularly towards the end of the process, time must be given for ch addition to produce its effect before a further quantity is ured in. When the operation is finished, the mixture will esent an olive green appearance, which, on standing a few inutes, will change to a golden brown. The last traces of the ue colour are best seen by drying the paper and examining it by nsmitted light, but a little experience will enable an unpractised e to judge by the appearance of the liquid; or if any uncertainty evails, a small quantity of the mixture may be taken out into a t-glass, and a drop of the reagent added, when, by comparing it th another portion in a similar glass, it will be seen whether any the blue colour remains.

When the brown colouring matter of the indigo interferes with e purposes to which it is to be applied, 10 grains should be dislved in sulphuric acid in the usual manner, and the solution being ade up to 1 pint, slips of stout blotting-paper are introduced into e blue liquid, and kept therein for ten minutes, and then dried. y subjecting indigo of known strength and purity to the same eatment, and comparing the results, it will be seen that those digoes which contain a large proportion of brown matter give a een tint to the paper, varying in intensity according to the amount esent.

From experiments made with pure indigo, the amount of biromate required to decolorise the blue solution is less when oxalic id is employed than when hydrochloric acid with heat is used.

2. By Potassic Ferricyanide (Ullgren).

This method is based upon the fact that red potassic prussiate destroys the blue colour of indigo in the presence of free alkali, by converting it into isatin, the reaction being formulated as follows:—

$$C^{16}H^{5}NO^{2} + 2K^{3}Fe^{2}Cy^{6} + 2KO = C^{16}H^{5}NO^{4} + 4K^{2}FeCy^{3}$$

The use of caustic soda or potash, however, is liable to cause a different reaction if used in varying quantity, and at higher temperature; it is therefore advisable to use sodic carbonate as the alkali.

Ullgren's description is as follows (Chem. Soc. Jour. 1865, 223):—

1. The quantity of sulphuric acid added to the solution of indigo should not be too great, and the temperature must not exceed 50°C, because, especially with impurer sorts of indigo, sulphurous acid in considerable quantity is then generated, and combinations with sulphuric acid are obtained, part of which are not dissolved in the acid liquid when diluted with water, like sulphopurpuric acid.

The quantity of sulphuric acid found most suitable, is ten times the weight of the indigotin and eight times that of the indigo, the acid itself being of the strength which is obtained when fuming sulphuric acid is mixed with distilled water until the mixture only is faintly fuming. With this strength of acid the formation of a certain portion of sulphopurpuric acid is of less consequence; only in measuring for titration, the diluted liquid must be well shaken.

2. The indigo solution should be very much diluted, and a sample preserved in order to serve as a guide as to the degree of dilution. To prepare the standard solution, 1 gm. of pure indigotin is dissolved in 10 gm. of sulphuric acid, mixed with water to 1 litre of liquid, and 10 c.c. of the solution thus obtained is also diluted to 1 litre of liquid; in this there are, consequently, 10 milligrammes of indigotin dissolved. The solution of indigotin to be tested should be so much diluted that it may be lighter than this sample-coloured solution.

3. The solution of sodic carbonate should be saturated in the cold. 20 c.c. of this solution is mixed with the quantity of indigo solution which has been measured and afterwards diluted to be titrated; it is so proportioned that its value of indigotin is about 10 milligrammes, but rather below than above this quantity.

4. The solution of potassic ferricyanide should also be very dilute. If 5·023 gm. of this salt is dissolved in 1 litre of water, then, with a certain quantity of sodic hydrate, 1 c.c. of this solution destroys 1 milligramme of indigotin. But if sodic carbonate is used in corresponding quantity, another reaction takes place, in consequence of which nearly a double quantity of ferricyanide is required. This, however, is of no consequence in practice, provided it is known how much of a solution of ferricyanide of given strength is required to destroy 1 milligramme of indigotin in solution,

rendered alkaline by sodic carbonate. The solution of ferricyanide used in the test experiments contained 2·5115 gm. of that salt in a litre, consequently 2 c.c. of it would just have changed 1 milligramme of indigotin into isatin.

5. When sodic carbonate is used, and the liquid is diluted to the degree above mentioned, the change of colour is shown in such a way that the blue colour gradually disappears, without distinctly changing into green, as is the case when the dilution is less. When the liquid has assumed a grey-yellow appearance, or generally when every tint of blue has disappeared, the operation may be regarded as complete.

The titration should be done slowly and with frequent stirring by a glass rod, and this is most easily done if the liquid is poured into a large porcelain basin, where also the change of colour can be most distinctly observed.

Examples:—1 gm. of pure indigotin was dissolved in 10 gm. of sulphuric acid, and the solution was diluted to 1 litre; 10 c.c. of this mixed in a porcelain vessel, with 1 litre of water and 20 c.c. of a cold saturated solution of sodic carbonate, required, of the solution of ferricyanide at a temperature of 18° C, in three experiments: 34·5, 35·35, 35·5 c.c.: mean 35 c.c.

1 gm. Bengal indigo, No. 1, which in the reduction, partly with grape-sugar, partly with ferrous sulphate and soda, was found to yield in even numbers 62 per cent. of indigotin, was dissolved in 8 gm. of sulphuric acid, and diluted with water to 1 litre; 10 c.c. of this mixed with $\frac{3}{4}$ of a litre of water and 20 c.c. of a solution of sodic carbonate saturated in the cold, required at a temperature of 18° C, in four experiments, 23, 22, 22·5 and 23 c.c. of the solution of ferricyanide: mean 22·6 c.c. But $35 : 22{\cdot}6 = 100 : x = 64{\cdot}4$ per cent. indigotin, consequently 2·4 per cent. more than was shown by reduction.

Similar approximate results, with 2 to 4 per cent. excess over those from the method of reduction, were obtained in experiments with several other kinds of indigo.

PART VI.

SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO COMPLETE QUANTITATIVE ANALYSIS.

ANALYSIS OF URINE.

§ 73. THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately, however, the most important matters, such as urea, sugar, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, and others, during the last few years, have resulted in a truer knowledge of this important secretion, and to the two first mentioned chemists we are mainly indebted for the simplest and most reliable methods of estimating its constituents. With the relation which the proportion of these constituents bear to health or disease, the present treatise has nothing to do, its aim being simply to point out the readiest and most reliable methods of determining them quantitatively. Their pathological importance is very fully treated by some of the authorities just mentioned, among the works of which Neubauer and Vogel's "Analyse des Harns," and Dr. Beale's, "Urine, Urinary Deposits, and Calculi," are most prominent and exhaustive, but above all we now have the collected experience of all the best authorities in the world in "The Pathological Handbook of Drs. Lauder Brunton, Klein, Foster, and Burdon Sanderson." (Churchill.)

The gramme system of weights and measures will be adopted throughout this section, while those who desire to use the grain system will have no difficulty in working, when once the simple relation between them is understood, see § 9, p. 19.* The question of weights and measures is, however, of very little consequence, if the analyst considers that he is dealing with relative parts or proportions only, and as urine is generally described as containing so many parts of urea, chlorides, or phosphates, per 1000, the absolute weight may be left out of the question. The grain system is more readily calculated into English ounces and pints, and therefore is generally more familiar to the medical profession of this country.

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* In a word, whenever c.c. occurs, dm. may be substituted; and in case of using grains for grammes, move the decimal point one place to the right—thus 7·0 grammes would be changed to 70 grains. Of course it is understood that where grammes are taken, c.c. must be measured, and with grains dm.; the standard solution being the same for both systems.

One thing, however, is necessary as a preliminary to the examination of urine, and which has not generally been sufficiently considered, that is to say, the relation between the quantity of secretion passed in a given time, and the amount of solid matters found in it by analysis. In a medical point of view, it is a mere waste of time, generally speaking, to estimate the constituents in half a pint or so of urine, passed at any particular hour of the day or night, without ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during, say 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; besides this, the analyst should register the colour, peculiarity of smell, if any, consistence, presence or absence of a deposit (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination), and lastly, its reaction to litmus should be observed.

1. Specific Gravity.

This is best taken by measuring 10 c.c. into an accurately tared beaker or flask, the increase of weight above 10 gm. will be the specific gravity, water being 1000. Where an accurate balance, pipette or weights are not at hand, a good urinometer may be used.

2. Estimation of Chlorides (calculated as Sodic Chloride).

This may be done in two ways, viz. :—

a. **By Silver (Mohr).** 10 c.c. of the urine are measured into a thin porcelain or platinum capsule, and 1 gm. of pure potassic nitrate in powder added; the whole is then evaporated to dryness, and gradually heated till the residue becomes white; it is then dissolved in a small quantity of water, and the potassic carbonate produced by the combustion of the organic matter, *nearly* neutralized by dilute nitric acid; two or three drops of solution of potassic chro-

mate are then added, and the mixture titrated with $\frac{N}{10}$ sil
§ 36.2. Each c.c. of silver solution represents 0·005846 g
consequently if 12·5 c.c. have been used, the weight of s
10 c.c. of urine is 0·073075 gm., and as 10 c.c. only were
weight multiplied by 10, or what amounts to the same
decimal point moved one place to the right, gives 7·3075
of salt for 1000 of urine.

In order to save calculation, it is convenient to measu
of the urine, add about ½ gm. of potassic nitrate, then
ignite, and titrate, as before directed; the number of c
silver used will represent the number of parts of salt in 1
of urine.

Example: 5·9 c.c. of urine passed by a patient suffer
Diabetes insipidus was evaporated and titrated as above,
3·1 c.c. silver solution, the proportion of salt was therefore
per 1000 of urine.

Pibram (Vierteljahrsh, f. pract. Heilk, 106, 101) ob
necessity for evaporating the urine with potassic nitrate
to titration by heating the urine with permanganate. 10 c.
are mixed with about 5 c.c. of $\frac{N}{10}$ permanganate, and 40 c.c.
then brought nearly to boiling; by this means a brown
precipitate is produced, consisting of organic matter and m
salt, which is filtered away, leaving the clear liquid col
that an excess of permanganate shows the rose tint at once
permanganate must be used to give this tint, which
removed by a few drops of oxalic acid solution, avoiding
and the fluid then titrated with $\frac{N}{10}$ silver solution and
as before described.

In cases where the urine is not highly coloured, it
possible to titrate it for chlorine by silver and chromat
evaporating with nitre; the phosphates do not interfere
whole of the chlorine is precipitated; the results obt
always slightly too high, owing to the colouring and
matter which carry down with them a little free silver.

b. **By Mercuric Nitrate (Liebig).** The principle
method is as follows:—If a solution of mercuric nitrate,
any excess of acid, is added to a solution of urea, a white
precipitate is produced, containing urea and mercuric oxi
proportion of 1 eq. of the former to 4 eq. of the latter (
Ur). When sodic chloride, however, is present in the
this precipitate does not occur, until all the sodic chlori
verted by double decomposition into mercuric chloride (

and sodic nitrate, the solution remaining clear; if the exact point be overstepped, the excess of mercury immediately produces the precipitate above described, so that the urea present acts as an indicator of the end of the process. It is therefore possible to ascertain the proportion of chlorides in any given sample of urine by this method, if the strength of the mercurial solution is known, since 1 eq. of mercuric oxide converts 1 eq. of sodic chloride into 1 eq. each of corrosive sublimate and sodic nitrate.

Although the details of this interesting process will be given here, long experience has convinced me that this method is far less accurate than the one previously given. Extreme care is required in the preparation and use of the mercurial solution, and even when these conditions are complied with, many cases occur in which the results obtained are totally incomprehensible; preference must therefore be given to the silver method. The strength of the standard solution of mercury is best arranged as follows:—

c. **Standard Solution of Mercuric Nitrate.** It is of great importance that the solution be pure, for if the mercury from which it is made be contaminated with traces of other metals, such as bismuth, silver, or lead, they will produce a cloudiness in the liquid while under titration, which may possibly hinder the exact ending of the reaction; therefore 18·42 gm. of the purest red oxide of mercury, or 17·06 gm. of pure metallic mercury (the former is preferable, as being easier to weigh and less likely to be impure) are put into a beaker, with a sufficiency of pure nitric acid of about 1·20 spec. grav. to dissolve it by the aid of a gentle heat; the clear solution so obtained is evaporated on the water bath to remove any excess of free acid. When the liquid is dense and syrupy in consistence, it may be transferred to the graduated cylinder or flask and diluted to a litre, 1 c.c. of the solution so prepared is equal to 0·01 gm. of sodic chloride, or 0·006065 gm. of chlorine. If on diluting the concentrated mercurial solution a yellow precipitate of basic mercuric nitrate should form, it must be allowed to settle, the clear liquid poured off, and a few drops of nitric acid added to the precipitate to redissolve it; the whole is then mixed and preserved for future use in a well stoppered bottle. It is always preferable to have this precipitate formed on dilution, as it is a proof of there being no excess of acid, which would considerably interfere with the accuracy of results.*

d. **The Baryta Solution.** Before urine can be submitted to titration by the mercurial solution, it is necessary to remove the phosphoric acid, and the proper agent for this purpose is a mixture composed of 1 volume of cold saturated solution of pure baric nitrate and 2 volumes ditto baric hydrate; the same agent is used previous to the estimation of urea, and may be simply designated "Baryta Solution."

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* Too great stress cannot be laid upon having this solution free from nitric acid in the uncombined state.

The Analytical process. 40 c.c. of the clear urine are mixed with 20 c.c. of baryta solution, and the thick mixture poured upon a small dry filter; when sufficient clear liquid has passed through, 15 c.c. = 10 c.c. of urine are taken with a pipette and just neutralized, if necessary, with a drop or two of nitric acid; if not alkaline, the probability is that sufficient baryta solution has not been added to precipitate all the phosphoric and sulphuric acids; this may be known by adding a drop or so of the baryta solution to the filtrate; if any precipitate is produced, it will be necessary to mix off a fresh quantity of urine with three-fourths or an equal quantity of baryta, in which case 17½ or 20 c.c. must be taken to represent 10 c.c. of the urine; the excess in either case of baryta must be *cautiously* neutralized with nitric acid.

The vessel containing the fluid in then brought under a **Mohr's** burette containing the mercurial solution, and small portions delivered in with stirring, until a distinct permanent precipitate is produced; it may happen that a turbidity is produced from the very first drop or two, owing to slight impurities in the mercurial solution; but as this will not increase, the point when the urea precipitate appears is not difficult to determine; the volume of solution used is then read off and calculated for 1000 parts of urine.

Example: 15 c.c. of the liquid prepared with a sample of urine, as described above (= 10 c.c. of urine) required 6·2 c.c. of mercurial solution, the quantity of salt present was therefore 0·062 gm., or 6·2 parts in 1000 parts of urine.

3. Estimation of Urea (Liebig).

The combination between urea and mercuric oxide in neutral or alkaline solutions has been alluded to in the foregoing article on chlorides; it will therefore probably be only necessary to say that the determination of urea in urine is based on that reaction; and as the precipitate so produced is insoluble in water or weak alkaline solutions, it is only necessary to prepare a standard solution of mercury of convenient strength, and to find an indicator by which to detect the point when all the urea has entered into combination with the mercury, and the latter slightly predominates. This indicator is sodic carbonate. If, in the course of adding the mercurial solution from the burette to the urine, a drop of the mixture be taken from time to time and brought in contact with a few drops of solution of sodic carbonate on a glass plate slab, or watch glass, no change of colour is produced at the point of contact until the free urea is all removed; when this is the case, and the mercury is slightly in excess, a yellow colour is produced, owing to the formation of hydrated mercuric oxide.

The compound of urea and mercury consists, according to Liebig's analysis, of 1 eq. of the former to four of the latter, that is to say, if the nitric acid set free by the mixture is neutralized from time to time with sodic carbonate or other suitable alkali. If this be not done, the precipitate first formed alters in character, and eventually consists only of 3 eq. of mercury with 1 of urea. In order to produce the yellow colour with sodic carbonate, there must be an excess of mercurial solution; theoretically, 100 parts of urea should require 720 parts of mercuric oxide; but practically, 772 parts of the latter are necessary to remove all the urea, and at the same time show the yellow colour with alkali, consequently the solution of mercuric nitrate must be of empirical strength, in order to give reliable results.

a. Preparation of the Mercuric Solution. 77·2 gm. of red mercuric oxide, or 71·5 gm. of the metal itself, are treated with nitric acid, as described in the previous article on chlorides, and in either case diluted to 1 litre, 1 c.c. of the solution is then equal to 0·01 gm. of urea. (The extreme care required to remove traces of foreign metals from the mercury is not so necessary here as in the foregoing instance, but no large amount of free acid must be present.) Dragendorff prefers to use mercuric chloride in the preparation of the standard solution, by weighing 96·855 gm. of the pure salt which is dissolved in water, then precipitated with dilute caustic soda, the precipitate well washed by decantation until free from chlorine, then dissolved in a slight excess of nitric acid, and the solution diluted to 1 litre.

The Analytical process. Two volumes of the urine are mixed with one of baryta solution, as before described in the case of chlorides (reserving the precipitate for the determination of phosphoric acid, if necessary), and 15 c.c. = 10 c.c. of urine, taken in a small beaker for titration; it is brought under the burette containing the mercurial solution (without neutralizing the excess of baryta, as in the case of chlorides), and the solution added in small quantities so long as a distinct precipitate is seen to form; a plate of glass laid over dark paper is previously sprinkled with a few drops of solution of sodic carbonate, and a drop of the mixture must be brought from time to time, by means of a small glass rod, in contact with the soda; so long as the colour remains white, free urea is present in the mixture; when the yellow colour is distinctly apparent, the addition of mercury is discontinued, and the quantity used calculated for the amount of urea. It is always advisable to repeat the analysis, taking the first titration as a guide for a more accurate estimation by the second.

Example: 15 c.c. of urine deprived of phosphates = 10 c.c. of the original urine was titrated as described, and required 17·6 c.c. of mercurial solution; consequently there was 0·176 gm. of urea present in the 10 c.c., or 17·6 parts in the 1000 of urine.

b. **Corrections and Modifications.** In certain cases the results obtained by the above method are not strictly correct, owing to the variable state of dilution of the liquids. The errors are, however, generally so slight as not to need correction. Without entering into a full description of their origin, I shall simply record the facts, and give the modifications necessary to be made where thought desirable.

The Urine contains more than 2 per cent. of Urea, *i.e.*, more than 20 parts per 1000. This quantity of urea would necessitate 20 c.c. of mercurial solution for 10 c.c. of urine; all that is necessary to be done when the first titration has shown that over 2% is present is to add half as much water to the urine in the second titration as has been needed of the mercurial solution above 20 c.c. Suppose that 28 c.c. have been used at first, the excess is 8 c.c., therefore 4 c.c. of water is added to the fluid before the second experiment is made.

The Urine contains less than 2% of Urea. In this case, for every 4 c.c. of mercurial solution less than 20, 0·1 c.c. must be deducted, before calculating the quantity of urea; so that if 16 c.c. have been required to produce the yellow colour with 10 c.c. urine, 15·9 is to be considered the correct quantity.

The Urine contains more than 1% of Sodic Chloride, *i.e.* more than 10 parts per 1000. In this case 2 c.c. must be deducted from the quantity of mercurial solution actually required to produce the yellow colour, with 10 c.c. of urine.

The Urine contains Albumen. In this case 50 c.c. of the urine are boiled with 2 drops of strong acetic acid to coagulate the albumen, the precipitate allowed to settle thoroughly, and 30 c.c. of the clear liquid mixed with 15 c.c. of baryta solution, filtered, and titrated for both chlorides and urea, as previously described.

The Urine contains Ammonic Carbonate. The presence of this substance is brought about by the decomposition of urea, and it may sometimes be of interest to know the quantity thus produced, so as to calculate it into urea.

As its presence interferes with the correct estimation of urea direct, by mercurial solution, a portion of the urine is precipitated with baryta as usual, and a quantity, representing 10 c.c. of urine, evaporated to dryness in the water-bath to expel the ammonia, the residue then dissolved in a little water, and the urea estimated in the ordinary way. On the other hand, 50 or 100 c.c. of the urine, not precipitated with baryta, is titrated with normal sulphuric acid and litmus paper, each c.c. of acid representing 0·017 gm. of ammonia, or 0·030 gm. of urea.

4. Estimation of Urea by its conversion into Nitrogen Gas.

If a solution of urea is titrated with an alkaline solution of hypochlorite or hypobromite, the urea is rapidly decomposed and nitrogen evolved which can be collected and measured in any of the usual forms of gas apparatus described in the section on analysis of gases.

Test experiments with pure urea have shown, that the whole of the nitrogen contained in it are eliminated in this process with the exception of a constant deficit of 8 per cent. In the case of urine, there are other nitrogenous constituents present, such as uric acid, hippuric acid, and creatinine, which render up a small proportion of their nitrogen in the process, but the quantity so obtained is insignificant, and may be disregarded. Consequently, for all medical purposes, this method of estimating urea in urine is sufficiently exact.

Russell and West (Chem. Soc. Jour., 2 ser., xii., p. 749), have described a very convenient apparatus for working the process and which gives very good results in a short space of time.

A drawing of the apparatus is given in the paper referred to and which may be verbally described as follows :—

The tube for decomposing the urine is about 9 inches long, and about half-an-inch inside diameter; at 2 inches from its closed end an elongated bulb is blown, leaving an orifice at its neck of ⅜ of an inch in diameter; the bulb should hold about 12 c.c.; the mouth of this tube is fixed into the bottom of a tin tray about 1¾ inch deep, which acts as a pneumatic trough; the tray is supported on legs long enough to allow of a small spirit lamp being held under the bulb tube; the measuring tube for collecting the nitrogen is graduated into cubic centimetres, and of such size as to fit over the mouth of the decomposing tube; one holding about 40 c.c. is a convenient size. Russell and West, have fixed by experiment the proportions so as to obviate the necessity for correction of pressure and temperature, namely, 37·1 c.c. = 0·1 gm. of urea, since they found that 5 c.c. of a 2 per cent. solution of urea constantly gave 37·1 c.c. of nitrogen at ordinary temperatures and pressures. The entire apparatus can be purchased of most operative chemists for a moderate sum.

Hypobromite Solution. This is best prepared by dissolving 100 gm. of common caustic soda in 250 c.c. of water and adding 25 c.c. of bromine; this mixture gives a rapid and complete decomposition of the urea.

The Analytical process. 5 c.c. of the urine are measured into the bulb tube, fixed in its proper position, and the sides of the tube washed down with distilled water so that the bulb is filled up to its constriction. A glass rod, having a thin band of india-rubber on its end, is then passed down into the tube so as to plug up the narrow opening of the bulb. The hypobromite solution is then poured into the upper part of the tube until it is full, and the trough is afterwards half filled with water.

The graduated tube is filled with water, the thumb placed on the open end, and the tube is inverted in the trough. The glass rod is then pulled out, and the graduated tube slipped over the mouth of the bulb-tube.

The reaction commences immediately, and a torrent of gas rises into the measuring tube. To prevent any of the gas being forced out by the reaction, the upper part of the bulb-tube is slightly narrowed, so that the gas is directed to the centre of the tube. With the strength of hypobromite solution, above described, the reaction is complete in the cold in about ten or fifteen minutes; but in order to expedite it, the bulb is slightly warmed. This causes the mixing to take place more rapidly, and the reaction is then complete in five minutes. The reaction will be rapid and complete only when there is considerable excess of the hypobromite present. After the reaction the liquid should still have the characteristic colour of the hypobromite solution.

The amount of constriction in the tube is by no means a matter of indifference, as the rapidity with which the reaction takes place depends upon it. If the liquids mix too quickly, the evolution of the gas is so rapid that loss may occur. On the other hand, if the tube is too much constricted, the reaction takes place too slowly.

The simplest means of supporting the measuring-tube is to have the bulb-tube corked into a well, which projects from the bottom of the trough about 1 inch downwards. The graduated-tube stands over the bulb-tube, and rests upon the cork in the bottom of the well. It is convenient to have, at the other end of the trough, another well, which will form a support for the measuring-tube when not in use.

To avoid all calculation, the measuring tube is graduated so that the amount of gas read off expresses at once what may be called the percentage amount of urea in the urine experimented upon, *i.e.*, the number of grammes in 100 c.c., 5 c.c. being the quantity of urine taken in each case. The gas collected is nitrogen saturated with aqueous vapour, and the bulk will obviously be more or less affected by temperature and pressure. Alterations of the barometer produce so small an alteration in the volume of the gas, that it may be generally neglected; *e.g.*, if there are 30 c.c. of nitrogen, the quantity preferred, an alteration of 1 inch in the height of barometer would produce an error in the amount of urea of about 0·003; but for more exact experiments, the correction for pressure should be introduced.

In the wards of hospitals, and in rooms where the experiments are most likely to be made, the temperature will not vary much from 65° F., and a fortunate compensation of errors occurs with this form of apparatus under these circumstances. The tension of the aqueous vapour, together with the expansion of the gas at this temperature, almost exactly counterbalances the loss of nitrogen in the reaction.

The authors found from experience that 5 c.c. of urine is the most advantageous quantity to employ, as it usually evolves a convenient bulk of gas to experiment with, *i.e.*, about 30 c.c. They have shown that 5 c.c. of a standard solution containing 2 per cent. of urea evolves 37·1 c.c. of nitrogen, and have consequently taken this as the basis of the graduation of the measuring-tube. This bulk of gas is read off at once as 2 per cent. of urea, and in the same way the other graduations on the tube represent percentage amounts of urea.

If the urine experimented with is very rich in urea, so that the 5 c.c. evolve a much larger volume of gas than 30 c.c., then it is best at once to dilute the urine with its own bulk of water, take 5 c.c. of this diluted urine, and multiply the volume of gas obtained by two.

If the urine contains much albumin, this interferes with the process so far that it takes a long time for the bubbles of gas to subside, before the volume of gas obtained can be accurately read off. It is therefore better in such cases to remove as much as possible of the albumin by heating the urine with two drops of acetic acid, filtering, and then using the filtra usual manner. The presence of sugar in the urine does the reaction.

5. Estimation of Phosphoric Acid.—See also § 69

This method is based on the fact that when a solution acetate is added to a fluid containing phosphoric acid, sod and free acetic acid, the whole of the phosphoric acid i down as uranic phosphate, having a light lemon colou composition 2 ($Ur^2 O^3$), P^2O^5 + Aq. The point at whic phosphoric acid is precipitated may be readily ascert bringing a drop of the yellow liquid in which the pro suspended in contact with a drop of solution of yellov prussiate on a white porcelain plate; an excess of uraniun immediately produces a brown colour at the point of cont yellow precipitate is quite insoluble in acetic acid, but rea any of the mineral acids; therefore if any of them shoul to bring the phosphates into solution they must be neut an alkali previously to adding the acetic acid and testing uranium solution. See fuller details in § 69.

The following solutions are required:—

1. **Standard Uranic Acetate,** containing about 4(uranic acetate in the litre, so that each c.c. equals about P^2O^5. This solution cannot well be prepared by wei acetate direct and dissolving, owing to the difficulty in the substances absolutely pure or with definite proportions in them. It is therefore necessary to graduate it upon sc phate by testing, as described in § 69.

2. **Standard Sodic Phosphate,** containing 25·2 gm. Each c.c. equals 0·05 gm. P^2O^5.

3. **Solution of Sodic Acetate** with free acetic acid to to urine in the proportion of 5 c.c. to every 50 c.c. is pr dissolving 100 gm. of sodic acetate in about 900 c.c. of water, and making up the solution to 1000 c.c. with con acetic acid.

4. **A Solution of Yellow Potassic Prussiate,** about 20 of water, freshly prepared, or some finely powdered pr

The Analytical process. 50 c.c. of the clear urine are into a small beaker, together with 5 c.c. of the solution acetate. The mixture is then warmed in the water bath, wise, and the uranium solution delivered in from the bur constant stirring, as long as a precipitate is seen to occur;

portion of the mixture is then removed with a glass rod, and tested as before described; so long as no brown colour is produced, the addition of uranium may be continued; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed; if it coincides with the original testing of the uranium solution with a similar quantity of fluid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 c.c. of urine; if the uranium has been used accidentally in too great quantity, 10 or 20 c.c. of the same urine may be added, and the testing concluded more cautiously. Suppose, for example, that the solution has been added in the right proportion, and 19·2 c.c. used, the 50 c.c. will have contained 0·096 gm. phosphoric acid. With care and some little practice the results are very satisfactory.

Earthy Phosphates.

The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200 c.c. of the urine are measured into a beaker, and rendered freely alkaline with ammonia; the vessel is then set aside for ten or twelve hours, for the precipitate of earthy phosphates to settle: the clear fluid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water; a hole is then made in the filter and the precipitate washed through, the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid, some sodic acetate added, and the mixture titrated as before described; the quantity of phosphoric acid so found is deducted from the total previously estimated, and the remainder gives the quantity existing in combination with alkalies.

6. Estimation of the Sulphuric Acid.

Standard Baric Chloride. A quantity of crystallized baric chloride is to be powdered, and dried between folds of blotting-paper. Of this, 30·5 gm. are dissolved in distilled water, and the liquid made up to 1000 c.c. 1 c.c.$=$0·01 gm. of SO^3.

A dilute solution of *sodic sulphate* is also required.

The Analytical process: 100 c.c. of the urine are poured into a beaker, a little hydrochloric acid added, and the whole placed on a small sand-bath, to which heat is applied. When the solution boils, the baric chloride is allowed to flow in very gradually as long as the precipitate is seen distinctly to increase. The heat is removed, and the vessel allowed to stand still, so that the precipitate may subside. Another drop or two is then added, and so on, until the whole of the SO^3 is precipitated. Much time, however, is saved by using the little apparatus represented in fig. 25. A little of the fluid is thus filtered clear, poured into a test-tube, and tested with a drop from the burette; this is afterwards returned to the beaker, and more of the test solution added, if necessary. The operation is repeated until the precipitation is complete. In order to be sure that too much of the baryta-solution has not been added, a drop of the clear fluid is added to the solution of sodic sulphate placed in a test-tube or upon a plate of black glass, see § 40.3. If no precipitate occurs, more baryta must be added; if a slight cloudiness takes place, the analysis is finished; but if much precipitate is produced, too large a quantity of the test has been used, and the analysis must be repeated.

For instance, suppose that 18·5 c.c. have been added, and there is still a slight cloudiness produced which no longer increases after the addition of another half c.c., we know that between 18½ and 19 c.c. of solution have been required to precipitate the whole of the sulphuric acid present, and that accordingly the 100 c.c. of urine contain between 0·185 and 0·19 gm. of SO^3.

7. Estimation of Sugar.

Fehling's method is precisely the same as described in § 71.1.

The Analytical process: 10 c.c. of the clear urine are diluted by means of a measuring flask to 200 c.c. with water, and a large burette filled with the fluid; 10 c.c. of the copper solution (=0·05 gm. of sugar) are then measured into a white porcelain capsule, 40 c.c. of distilled water added, the vessel arranged over a spirit or gas lamp under the burette, and brought to boiling; the diluted urine is then delivered in cautiously from the burette until the bluish colour has nearly disappeared. The addition of the urine must then be continued more carefully, allowing the red precipitate to subside after each addition by removing the heat, when by gently sloping the capsule, the clear liquid allows the white sides of the capsule to be seen, so that the faintest shade of blue would be at once perceptible. When the colour is all removed, the burette is read off, and the quantity of sugar in the urine calculated as follows:—

Suppose that 40 c.c. of the diluted urine have been required to reduce the 10 c.c. of copper solution, that quantity will have contained 0·05 gm. of sugar; but, the urine being diluted 20 times,

.e 40 c.c. represent only 2 c.c. of the original urine; therefore c.c. of it contain 0·05 gm. sugar, or 25 parts per 1000.

Knapp's method, which is equally applicable to urine, is scribed in § 71.2.

8. Estimation of Uric Acid.

The determination of uric acid in urine is not often considered much consequence, there are, however, circumstances under iich it is desirable, especially in urinary deposits. As the antity present in urine is very small, it is necessary to take, say m 300 to 500 c.c. for the estimation.

The urine being measured into a beaker, from 5 to 8 c.c. of pure drochloric acid are added, the whole well mixed, covered with a ss plate, and set aside in a cool place for 24 or 30 hours; at the d of that time the uric acid will be precipitated in small crystals, on the bottom and sides of the beaker, the supernatant liquid is canted, washed once with cold distilled water, then dissolved in mall quantity of pure solution of potash, diluted to 6 or 8 ounces th distilled water, acidified strongly with sulphuric acid, and rated precisely as oxalic acid, § 28.4, with $\frac{N}{10}$ permanganate, each . of which is equal to 0·0075 gm. of uric acid. This method is t absolutely correct, owing to the fact that with the uric acid ere is always precipitated a certain amount of colouring matter of e urine, which destroys the permanganate equally with the uric d. The method by weighing is, however, open to the same jection, beside being very troublesome, so that no advantage is ined by the latter plan. **Hassall** states that the normal quany of uric acid in urine has hitherto been considerably underimated, and that if the urine is concentrated by evaporation fore precipitating with hydrochloric acid, a much larger quantity ll be obtained. See *Lancet*, Feb. 1865.

9. Estimation of Lime and Magnesia.

100 c.c. of the urine are precipitated with ammonia, the preitate redissolved in acetic acid, and sufficient ammonic oxalate led to precipitate all the lime present as oxalate; the precipitate allowed to settle in a warm place, then the clear liquid passed ough a small filter, the precipitate brought upon it, washed with water, the filtrate and washings set aside, then the precipitate, ether with the filter, pushed through the funnel into a flask, ne sulphuric acid added, the liquid freely diluted, and titrated h permanganate, precisely as in § 49; each c.c. of $\frac{N}{10}$ permanate required represents 0·0028 gm. of lime (Ca O).

nstead of the above method the following may be adopted:—

The precipitate of calcic oxalate, after being washed is dried, and together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of calcic oxide and carbonate. It is then transferred to a flask by the aid of the washing bottle, and an excess of normal nitric acid delivered in with a pipette; the amount of acid, over and above what is required to saturate the lime, is found by normal caustic alkali, precisely as described in § 20, each c.c. of normal acid being equal to 0·028 gm. of lime.

In examining urinary sediment or calculi for calcic oxalate, it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate, as in § 28.4; each c.c. of $\frac{N}{10}$ permanganate represents 0·0054 gm. of calcic oxalate.

Magnesia. The filtrate and washings from the precipitate of calcic oxalate are then made alkaline with ammonia, sodic phosphate added, and set aside for 8 or 10 hours in a slightly warm place, that the magnesia may separate as double magnesic and ammonic phosphate; the supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranium solution, as in § 69; each c.c. of solution required represents 0·002815 gm. of magnesia.

10. Ammonia.

The only method hitherto applied to the determination of ammonia in urine is that of Schlösing, which consists in placing a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of titrated acid. In the course of from 24 to 36 hours, all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea being decomposed into free ammonia, when heated with alkali; there is also the uncertainty as to the completion of the process, and if the vessel be opened before the absorption is perfect, the analysis is spoiled. The following plan is recommended as in most cases suitable:—When a solution containing salts of ammonia is mixed with a measured quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved, § 17; that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has left to go free. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the estimation of the original amount of ammoniacal salts. The decomposition is such that while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and as this reacts equally as alkaline as though it were free potash, it does not interfere in the slightest degree with the estimation of the original ammonia.

The following is the best method of procedure:—

100 c.c. of the urine are exactly neutralized with normal alkali, as in the following article, for the estimation of free acid; it is then put into a flask capable of holding five or six times the quantity; 10 c.c. of normal alkali added, and the whole brought to boiling, taking care that the bladders of froth which at first form do not boil over; after a few minutes these subside, and the boiling proceeds quietly; when all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly: the contents then emptied into a tall beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought into contact with neutral or violet coloured litmus paper produces neither a blue nor red spot; the number of c.c. of normal acid are deducted from the 10 c.c. of alkali, and the rest calculated as ammonia. 1 c.c. of alkali=0·017 gm. of ammonia.

Example: 100 c.c. of urine were taken, and required 0·7 c.c. of normal alkali to saturate its free acid; 10 c.c. of alkali were then added, and the mixture boiled until a piece of moistened red itmus paper was not turned blue when held in the steam; 4·5 c.c. of normal acid were afterward required to saturate the free alkali; he quantity of ammonia was therefore equal to 5·5 c.c., which multiplied by 0·017 gave 0·0935 gm. in 1000 of urine.

It must be borne in mind that the plan just described is not applicable to urine which has already suffered decomposition by ge or other circumstances so as to contain carbonate of ammonia; n this case it would be preferable to adopt Schlösing's method; r where no other free alkali is present, direct titration with normal cid may be adopted.

11. Estimation of Free Acid.

The acidity of urine is doubtless owing to variable substances, among the most prominent of which appear to be acid sodic phosphate and lactic acid, other free organic acids are probably in many cases present; under these circumstances, the degree of acidity cannot be placed to the account of any particular body; nevertheless, it is frequently desirable to ascertain its amount, which is best done as follows:—

100 c.c. of the urine are measured into a beaker, and normal alkali, delivered in drop by drop from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper, produces no change of colour; the degree of acidity is then registered as being equal to the quantity of normal alkali used.

12. Estimation of Albumen.

a. By Weight. 100 c.c. of the clear urine, or less than that quantity if much albumen is present, the 100 c.c. being made up with water, are introduced into a good-sized beaker, and heated in the water bath for half an hour. If the urine is sufficiently acid, the albumen will be separated in flocks. Should this not be the case at the end of the half-hour's heating, and the fluid merely appears turbid, one or two drops (not more, unless the urine is alkaline) of acetic acid are added, and the heating continued until the albumen separates in flocks; the beaker is then put aside till the precipitate has settled, and the clear liquid passed through a small filter (previously dried at 212°, then cooled between two watch glasses held together with a spring clip, and weighed); the precipitate is then washed with a little hot water, and brought upon the filter without loss, the beaker washed out with hot distilled water, and the last traces of precipitate loosened from the sides with a feather. The filter with its contents is then repeatedly washed with hot water, until a drop of the filtrate evaporated on a piece of glass leaves no residue. The funnel containing the filter is then put into a warm place to dry gradually; lastly, the filter removed into one of the watch glasses and dried thoroughly in the air bath at 110°C., or 220° Fahr.; another watch glass is then covered over that containing the filter, the spring clip passed over to hold them together, the whole cooled under the exsiccator and weighed; the weight of the glasses, filter, and clip, deducted from the total, gives the weight of albumen in 100 c.c. of urine.

b. By Measure. In order to avoid the tedious process of estimating the albumen as just described, Bödeker has devised a method of titration which gives very fair approximate results when ıuantity of albumen is not too small, say not less than 1½ to r cent. The principle is based on the fact that potassic ferroide completely precipitates albumen from an acetic acid solution ıe atomic proportions of 211 ferrocyanide to 1612 albumen. ıe standard solution of ferrocyanide is made by dissolving) gm. of the pure salt in a litre of distilled water. 1 c.c. of olution so prepared precipitates 0·01 gm. of albumen.

.e Analytical process: 50 c.c. of the clear filtered urine are d with 50 c.c. of ordinary commercial acetic acid, and the fluid nto a burette. Five or six small filters are then chosen, of close .re, and put into as many funnels, then moistened with a few ı of acetic acid, and filled up with boiling water; by this s the subsequent clear filtration of the mixture is considerably tated. 10 c.c. of the ferrocyanide solution are then measured a beaker, and 10 c.c. of the urinary fluid from the burette 1, well shaken, and poured upon filter No. 1. If the fluid h passes through is bright and clear with yellowish colour, the :yanide will be in excess, and a drop of the urine added to it produce a cloudiness. On the other hand, if not enough :yanide has been added, the filtrate will be turbid, and pass ıgh very slowly; in this case, frequently both the ferrocyanide :he urine will produce a turbidity when added. In testing iltrate for excess of ferrocyanide, care must be taken not to ıoo much of the urine, lest the precipitate of hydroferrocyanide ɔumen should dissolve in the excess of albumen.

:cording to the result obtained from the first filter, a second is made increasing the quantity of urine or ferrocyanide half much again, and so on until it is found that the solution first n to be in excess is reversed; a trial of the mean between ıuantity and the previous one will bring the estimation closer, at a final test may be decisive.

:ample: 50 c.c. of urine passed by a patient suffering from ht's disease, were mixed with the like quantity of acetic and tested as follows:—

	Urine.	Ferrocyanide.	In filtrate Urine.	In filtrate Ferrocyanide. gave
1.	10 c.c.	10 c.c.	0	prec.
2.	10 „	20 „	prec.	0
3.	10 „	15 „	0	prec.
4.	10 „	17·5 „	0	faint prec.
5.	10 „	18 „	0	0

ıfore, the 10 c.c. of diluted urine=5 c.c of the original secrecontained 0·18 gm. albumen, or 36 parts per 1000.

13. Estimation of Soda and Potash.

c.c. urine are mixed with the same quantity of baryta solu-allowed to stand a short time, and filtered; then 80 c.c. = 40 c.c. urine, measured into a platinum dish, and evaporated to dryness in the water-bath ; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, ammonic carbonate added so long as a precipitate occurs, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and ammonic carbonate, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed sodic and potassic chlorides is obtained ; the proportion of each is found by titrating for the chlorine, as in § 37, and calculating as there directed under the head of "mixed alkaline chlorides."

14. Estimation of Total Solid Matter.

The correct determination of the total solid matter is a very difficult task, owing to the fact that, on the one hand, the residue is very hygroscopic, and, on the other, that a partial decomposition of the urea takes place by heating it to a sufficient temperature to expel all the water. A tolerably satisfactory plan is to measure 5 c.c. into a shallow platinum or porcelain capsule, which is placed beside a vessel of strong sulphuric acid, under the receiver of a powerful air-pump, and kept *in vacuo* until all moisture is removed.

A rough estimation may be made by evaporating 10 or 20 c.c. of the urine on the water-bath, then drying in the air-bath at 115° C. or 230° Fahr., until the weight remains tolerably constant.

The only *correct* method is to introduce a measured portion of the urine, not more than 2 or 3 c.c. (contained in a small boat-shaped capsule, filled with fragments of glass), into a wide glass tube passing through boiling water, to one end of which is attached an aspirator, to the other a chloride of calcium tube ; between the aspirator and the tube containing the urine a small flask is inserted, containing a measured quantity of normal sulphuric acid, so that any ammonia, given off in the evaporation, is retained, and its quantity afterwards found by titration with normal alkali ; it is then calculated into urea, and its weight added to the dry residue actually found. For further details see Neubauer's paper (Zeitschrift für an. Chemie, vol. ii, p. 166).

15. Estimation of the Total Saline Matter.

A measured portion of the urine, say 10 c.c., are evaporated to dryness in a small porcelain crucible, about 10 drops of nitric acid added, and the crucible gradually heated to dull redness; it is then suffered to cool, and the same quantity of nitric acid again added; then heated up again gradually to a moderately strong heat until all the carbon is destroyed and the residue white; it is then cooled and weighed.

ANALYSIS OF SOILS.

§ 74. THE following instructions for the examination of soils are not given so much for the use of practised scientific chemists, as for the guidance of those who may not have the advantage of a complete laboratory, or who may only desire to estimate some of the principal constituents of a soil.

The instructions for mechanical analysis, the importance of which cannot be overrated, are taken from Dr. Noad's article on soils in the "Chemist and Druggist."

1. Mechanical Analysis of a Soil.

a. **Selection of the Sample.** Too much care cannot be taken to obtain a fair average specimen. For this purpose one or two pounds should be taken from each of four or five different parts of the field where the soil appears to be nearly the same. These should be well mixed together, and a pound or so selected for analysis; all samples should be kept in well-corked bottles. It is not unfrequent to see in a field, otherwise fertile, a few patches almost barren, where plants, especially when the field is in white crop, spring up, and for a time look quite healthy, but soon become diseased, assume a yellow colour, and die. Specimens from such parts should on no account be mixed with the rest; they should be examined by themselves, and the results compared with those given by the fertile parts; by following this course the cause of sterility and the means of curing it are most likely to be discovered.

b. **Determination of Water.** Spread a weighed quantity (say half a pound) of the soil upon a sheet of white paper, and expose it to the air in a dry room for several hours, weighing it at intervals of two or three hours till the weight remains constant; the loss indicates the amount of water which has evaporated, but by no means the whole of the water which the soil contains. To determine which, heat about 500 grains of the air-dried soil in a small glass beaker plunged into an oil bath, the temperature of which is kept between 150–160° C. (300°–350° Fahr.), till it ceases to lose weight, the result gives a close approximation to the amount of water. *Absolute* desiccation cannot, however, be accomplished except at a heat close upon redness, which is, of course, inadmissible, as the organic matters the soil contains would thereby become altered or destroyed.

c. **Absorbing power.** Allow the 500 grains of soil dried as above to cool in a covered vessel; then spread it out on a sheet of paper, and expose it to the air for 24 hours; note the increase of weight which is due to absorption of water, and if it amounts to 10 grains, it is so far an indication of great agricultural capability.

d. **Power of holding Water.** Put 1000 grains of air-dried soil into a filter enclosed in another, placed in a funnel; pour cold water, drop by drop, on the soil until it begins to trickle down the neck of the funnel; cover with a piece of glass, and allow it to stand for an hour or two, adding a few drops of water from time to time until it is certain that the whole soil is perfectly soaked; remove the filters from the funnel, and open them upon a linen cloth to remove the drops of water adhering to the paper. The outside filter is now placed in one pan of the balance, and the inner one containing the soil on the other; and the whole being carefully balanced, the true weight of the wet soil is obtained. Suppose this to be 1400, then the soil is capable of holding 4 per cent. of water.

e. **Rapidity of Drying.** Expose the soil with its filter on the plate to the air for 4, 12, or 24 hours, weighing from time to time. The loss of weight, indicating the tendency of the soil to dry, may convey useful information as to the necessity or otherwise of drainage.

f. **Relative proportions of Gravel, Sand, and Clay.** Rub a quantity of air-dried soil between the hands, and remove and weigh any *stones* which may be present. Weigh off 4000 grains, and pass them through a sieve (No. 1) of copper wire gauze, the meshes of which are about $\frac{1}{10}$th of an inch in diameter. Remove the sieve from its bottom, and place it over a deep evaporating basin; throw a gentle stream of water upon the contents, and stir with a spatula or the hand until the water passes through clear. Transfer the residue to another basin, and place it in the water-oven to dry; then weigh, after which ignite in the air, and when cold weigh again. The first weighing gives the amount of *coarse gravel*, and the second indicates the proportion of *organic matter* which this gravel contains. Transfer the soil which has passed through sieve No. 1 to sieve No. 2, the meshes of which are about $\frac{1}{10}$th of an inch in diameter, treat the residue on the sieve precisely as before, dry at 212°, weigh, ignite, and weigh again; the results give the amount of *gravelly sand*, and of organic matter mixed with it. Dry a portion of the soil which has passed through sieve No. 2 in the water oven, and weigh off 500 grains; transfer to a deep basin or flask, and boil for 20 minutes or so with water. The boiling must be continued until all the particles are thoroughly separated from each other. The *coarse sand*, *fine sand*, and *finely divided particles* are then separated from each other by the following simple process, recommended by Schultz:—The boiled soil is allowed to cool, and is then washed into an *elutriating glass*, which is merely a tall champagne glass 7 or 8 inches deep, and about 2¾ inches wide at the mouth, round which is fastened a brass ring about half an inch broad, with a tube slightly inclined downwards proceeding from its side. A gentle stream of water is caused to pass continuously into the elutriating glass in such a manner as to cause a constant agitation of the particles, whereby the finest are washed away through the tube at the top of the glass, and received in a beaker or any other convenient vessel. This stream of water is best kept up and regulated by causing it to flow from a reservoir provided with a stop-cock, to which is attached a tube funnel from 12 to 18 inches long, drawn out to a point, with a fine aperture. The end of this tube is placed nearly at the bottom of the elutriating glass, and the supply of water so adjusted that the funnel tube always remains half full of water. When the water runs off from the discharge tube nearly clear, the stop-cock of the reservoir is closed, and the elutriating glass being removed, the water is decanted from it, and it is washed into a small dish, where it is dried and weighed, after which it is ignited and weighed again; the two weights give the proportion of *coarse sand* and its *organic matter*. The elutriated turbid fluid is allowed to stand for several hours, and the water is then poured off into another beaker. The deposited matter, consisting of *fine sand* and *fine soil*, is then subjected to a second elutriating process, conducted as before, except that the force and volume of the washing water is considerably lessened. The operation is continued until the wash water passes off quite clear; this sometimes takes three or four hours, but it is, with the arrangement described, a self-acting process, requiring no personal superintendence. The residue in the elutriating glass is *fine sand*, which, with its organic matter, is estimated as before, by drying, weighing, igniting, and re-weighing. We have only now to deduct from the original 500 grains the quantities of *coarse* and *fine sand*, to obtain the proportion of finely-divided matter. The results of this mechanical analysis may be tabulated thus (Schultz):—

100 parts of the soil, dried at 100° C., contain (for example)——

		Fixed Substances.	Combustible or Volatile Substances.
6·90	Gravel (coarse)	6·90	0·00
	Organic matter	...	...
7·10	Gravel (fine)	6·43	...
	Organic matter	...	0·67
35·50	Sand (coarse)	34·37	...
	Organic matter	...	1·13
40·00	Sand (fine)	38·50	...
	Organic matter	...	1·50
10·50	Fine soil	9·50	...
	Organic matter, ammonia, and combined water . .	...	1·00
100·00		95·70	4·3

Stones, 2·10 per cent.

This mechanical treatment of soils is of high importance, and it is to be regretted that so few of our English soils have hitherto been so examined. The same remark applies to the analysis of *clays*. The operations above described apply equally to *clays* and to *soils*, except that in the case of clays we have not to look for *gravel*.

To render the matter complete, however, the gravel and sand should be moistened and examined under the microscope, with the view of ascertaining if they are wholly siliceous, or if they contain also fragments of different kinds of rock—sandstones, slates, granites, traps, limestones, or ironstones. A few drops of strong hydrochloric acid should also be added, when the presence of limestone is shown distinctly by an effervescence; of peroxide of iron by the brown colour which the acid speedily assumes; and of black oxide of manganese by the smell of chlorine, which is easily recognized.

g. **Determination of the Density of a Soil.** Dry a sample of the soil (from which the large stones have been picked out) at 100° C. in the water oven till it ceases to lose weight. Fill a perfectly clean and dry common phial with distilled water up to a mark made with a file on the neck, and weigh it carefully. Pour out part of the water, and introduce into the bottle in its stead 1000 grains of the dried soil; shake the bottle well, to allow the air to escape from the pores of the soil; fill up again with water to the mark on the neck, and again weigh. The weight of the soil divided by the difference between the weight of the bottle with soil and water, and the sum of the weights of soil and the bottle of water together, gives the density or specific gravity. Example—

	Grains.
The bottle with water alone weighs	2000
The dry soil	1000
Sum (being the weight which the bottle with the soil and water *would have had*, could the soil have been introduced without displacing any of the water)	3000
Actual weight of soil and water	2600
Difference (being the weight of water taken out to admit 1000 grains of soil)	400

Therefore, 1000 grains of soil have the same *bulk* as 400 grains of water—*i.e.*, the soil is 2½ times heavier than the water, since $\frac{1000}{400} = 2\cdot5$, its specific gravity.

h. **Determination of the Absolute Weight.** Weigh an exact imperial half-pint of the soil in any state of dryness. When this weight is multiplied by 150 it will give very nearly the weight of a cubic foot of the soil in that state.

2. Chemical Analysis.

The accurate and complete quantitative analysis of soils is a work of some difficulty, and cannot be entirely accomplished by volumetric means. Many of the principal substances, however, may be estimated in this manner, and the following method of procedure is given as the most convenient :—

1. **Water.** 250 grains of the air-dried sifted soil are weighed in a porcelain, platinum, or iron crucible, and heated for a con-

siderable time in the water bath till the weight is constant. The loss represents the amount of water.

2. **Organic matter.** 50 grains of the residue from 1 are ignited in a platinum or porcelain crucible until all the organic matter is destroyed; the residue is then suffered to cool, moistened with solution of carbonate of ammonia (to re-carbonate any lime), then dried in the air bath at about 150° C., or 300° Fahr.; the loss indicates the amount of organic matter in the perfectly dry soil, which is then calculated for 100 parts of air-dried soil.

3. **Carbonic Acid.** 50 grn. of the air-dried soil are introduced into the apparatus, fig. 20, and the carbonic acid estimated as in § 24.

4. **Chlorine.** 250 grn. of the air-dried soil are burnt in a platinum crucible, then cooled and moistened with a solution of potassic nitrate, again heated gently to dryness, then ignited again. The cold residue is then lixiviated with boiling water, filtered, the filtrate neutralized with acetic acid, and a measured portion of it titrated with $\frac{N}{10}$ silver and chromate, as in § 36.2.

5. **Oxide of Iron.** The insoluble residue of 4=250 grn. soil, is heated in the water bath with pure hydrochloric acid to extract all soluble matter, the solution filtered off, the residue washed with boiling water on a filter (residue preserved for future examination), and the filtrate and washings collected and diluted to 500 dm.; 200 dm.=100 grn. soil, are then taken, heated with a little nitric acid to peroxidise all the iron, and ammonia added in excess, so as to precipitate all oxide of iron and alumina; if the latter be required to be estimated, the precipitate must be collected on a filter, well washed, putting the filtrate and washings aside, then dried, ignited, and weighed; the residue, consisting of oxide of iron and alumina, with whatever traces of phosphoric acid there may be, is redissolved in a little hydrochloric acid, the solution treated with zinc, diluted considerably, and titrated with $\frac{N}{10}$ bichromate, § 31, for ferric oxide; the quantity so found deducted from the total weight of the precipitate gives the alumina and phosphoric acid. Should the estimation of alumina not be required, the precipitate need not be ignited, but simply redissolved with hydrochloric acid on the filter and titrated at once for iron. Should any portion of the iron in the original soil exist as protoxide, a weighed quantity, say 100 grains, of the fresh, sifted, and non-ignited soil, is exhausted with pure hydrochloric acid, the solution filtered and titrated direct with bichromate.

6. **Lime.** The filtrate and washings from 5 = 100 grn. soil, are mixed with ammonic oxalate in excess, the solution set aside in a warm place for an hour or so, the precipitate then collected on a filter, well washed, dried, and together with the filter ignited. The mixture of carbonate and caustic lime thus obtained is dissolved in an excess of normal nitric acid, and titrated as in § 49; calculation for lime to be made as there directed.

7. **Magnesia.** The filtrate and washings from 6 = 100 grn. soil, which if bulky, must be evaporated somewhat in the water bath, is to be made freely alkaline with ammonia, ammonic arsenate added in slight excess, and the solution set aside for twelve hours in the cold, that the magnesia may be precipitated as double ammonic and magnesic arsenate. The precipitate collected on a filter well washed with ammoniacal water (filtrate and washings set aside), redissolved on the filter with acetic acid, and the solution titrated with uranium, as in § 69. 1 dm. of standard uranium solution = 0·05 grn. P^2O^5, represents 0·02815 grn. MgO.

8. **Alkalies.** The filtrate and washings from 7 = 100 grn. soil, containing the alkalies as chlorides, together with ammonic chloride and a small quantity of ammonic arsenate, is evaporated to dryness on the water bath, then ignited gently and carefully under a chimney to volatilize all the arsenate and other salts of ammonia. The alkalies are then left nearly pure as chlorides; the residue is dissolved in a very little water, filtered through a small filter into a small crucible, evaporated to dryness, and weighed direct. If it be desirable to ascertain the amount of potash, it may be separated by weight as potassio-platinic chloride, or the indirect method of calculation, as in § 37, may be adopted.

9. **Phosphoric Acid.** The remainder of the acid solution, viz., 300 dm. = 150 grn. soil, is mixed with a little nitric acid, heated and precipitated with ammonia, as in 5, the precipitate collected on a filter and washed with boiling water (filtrate and washings set aside); the precipitate is then dissolved on the filter with dilute nitric acid, the filter slightly washed, and the solution so obtained digested in the water bath for twenty-four hours with about two ounces of molybdic solution prepared as directed § 69, page 225.

If any precipitate occurs, it will contain all the phosphoric acid (unless it should exist in large quantity, which is not probable) as ammonic phospho-molybdate, which is to be collected on a small filter, well washed with the same fluid, then redissolved in ammonia, and a portion of the magnesia mixture added, § 69, to precipitate the phosphoric acid as double ammonio-magnesic phosphate; the precipitate so produced is dissolved in acetic acid, and titrated with uranium as in § 69.

10. **Sulphuric Acid.** The filtrate and washings from 9 = 150 grn. soil are diluted up to a definite measure, and a convenient portion titrated for sulphuric acid by any of the methods given in § 40.

11. **Ammonia.** From 200 to 500 grains of the fresh air-dried soil are introduced into the distilling flask (fig. 19), together with a little water and a small piece of bees' wax (to prevent frothing); the tube *d* is filled with strong caustic potash or soda, the whole of which is allowed to run into the flask as soon as the heating commences. In all other respects the operation is conducted as described in § 17.

12. **Nitrogen.** 100 grains of the soil are dried at 150° C., and when cold mixed with soda lime in a combustion tube, and ignited as usual. The ammonia evolved may be received into normal sulphuric acid, and the mixture afterwards titrated with normal alkali in the usual manner; or dilute hydrochloric acid may be used in the bulb apparatus, the fluid evaporated to dryness on the water bath, then heated in the air bath to 120° C., and the residual ammonic chloride titrated as in § 36.2.

13. **Residue insoluble in Hydrochloric Acid.** The insoluble matter which has already been collected, as in 5 = 250 grn. soil, and consisting mainly of insoluble silicate of alumina and sand, is transferred to a platinum or porcelain dish or large crucible, dried and mixed with sulphuric acid of about 1·6 sp. gr. in excess; the mixture is left to digest somewhat, then heated slowly under a hood, to drive off all the free acid; the residue is then cooled, lixiviated with water, filtered, and the filtrate precipitated with ammonia; the precipitate may be washed, dried, ignited, and weighed as "Alumina insoluble in hydrochloric acid." The insoluble residue will consist of pure quartz sand.

ANALYSIS OF MANURES.

1. Guano.

§ 75. 1. **Moisture.** 100 grains, weighed in a platinum or porcelain crucible, are dried in the water bath till the weight is constant; the loss gives the percentage of moisture. It must, however, be borne in mind that in drying guano very often a loss of ammonia takes place; this can only be avoided by drying the sample in a current of warm air by means of an aspirator, and passing the air so flowing over the surface of the guano through normal acid in a bulb tube.

2. **Total Fixed Constituents.** Residue of 1 (= 100 grains of guano) is ignited at a low red heat till all organic matter is destroyed, and the residue is of a white or greyish colour; the weight so found gives the percentage of fixed constituents, which will act as a control over the subsequent analysis.

3. **Sand, Clay, or other Insoluble Matter.** Residue of 2 is boiled with dilute hydrochloric acid (which should not cause any amount of effervescence) till all soluble matter is extracted; the residue brought on a filter, washed, dried, ignited, and weighed, gives the percentage of insoluble matter. The filtrate and washings containing all the soluble matters are diluted up to a definite measure, say 500 dm.

4. **Phosphoric Acid as Insoluble Phosphates.*** 200 dm. of the solution prepared as in 3 (=40 grains of guano) are precipitated with ammonia in excess, the precipitate of phosphate of lime and magnesia redissolved in acetic acid, and the solution divided in half, one portion being titrated with uranium for total phosphoric acid, as in § 69, the remainder set aside for

5. **Lime.** To half of the acetic acid solution prepared as in 4, sufficient ammonic oxalate is added to precipitate all the lime; after standing an hour or so, the supernatant liquid is filtered off, and the precipitate washed (reserving the filtrate and washings), then dissolved and titrated as in § 57.

6. **Magnesia.** The filtrate and washings from 5 are rendered alkaline with ammonia, set aside for twelve hours, the precipitate of double phosphate of magnesia and ammonia collected, dissolved, and titrated as in § 74.7.

7. **Alkalies.** The filtrate and washings from 6 are mixed with sufficient baryta water to remove all the phosphoric and sulphuric

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* The amount of phosphoric acid existing as alkaline phosphates in a soluble form may be estimated separately in 1 gm. of guano simply exhausted with water and titrated with uranium. Gilbert has pointed out (Zeitschrift f. an. Chem. xii. 1) that in some kinds of rock guano there exist nodules of bicalcic phosphate; when such guano is ignited, the phosphoric acid becomes converted into pyrophosphoric acid, which would not be determined by the usual methods of analysis. When this is the case it is necessary to fuse the guano with a mixture of two parts of sodic carbonate and one of potassic chlorate, then dissolve the residue in nitric acid, neutralize with soda, add acetic acid and sodic acetate, and titrate with uranium as usual.

acids; the precipitate removed by filtration; the filtrate evaporated to a small bulk, and treated with ammonic hydrate and carbonate to remove excess of baryta, the filtrate and washings from this precipitate acidified with hydrochloric acid, evaporated to dryness, ignited, then redissolved in a small quantity of water, a few drops each of ammonia and ammonic carbonate added, filtered into a weighed platinum or porcelain crucible, the small filter thoroughly washed, and the filtrate and washings evaporated to dryness, ignited, and weighed as chlorides.

For the estimation of potash and soda contained in the mixture see § 37, which also contains rather more minute directions for the careful separation of the alkaline salts by the above method.

8. **Ammonia.** 10 grains of the guano, or more, if it be poor in ammonia, are boiled with caustic magnesia in the distilling apparatus, fig. 19, and the estimation of ammonia conducted as described in § 17. This gives the ready formed ammonia only.

9. **Nitrogen and Ammonia.** From 5 to 10 grains of the guano, according to its quality, are dried in the water bath and carefully mixed with soda lime, (previously coarsely powdered, heated, and cooled,) and the mixture introduced into a hard glass tube, closed at one end, about fourteen inches long and half-an-inch in diameter; the closed end is previously filled for about three-quarters-of-an-inch with a dried mixture of equal parts of oxalic acid and soda lime; on the top of this the mixture is placed about an inch of soda lime, then the mixture of guano and soda lime is filled in to within about two inches of the open end, and upon the top of it more plain soda lime; finally, a loose plug of dry asbestos is introduced, and a well fitting cork inserted, carrying the Varrentrapp and Will's bulb apparatus (filled to the proper extent with normal sulphuric acid). The tube is then wrapped round with a piece of iron or copper gauze, placed in the gas or charcoal combustion furnace, and gradually heated from its open end onwards until the ammonia is nearly all evolved; the whole tube is then strongly heated, and the heat brought especially to bear on the end containing the mixture of oxalic acid and soda lime; by this means a strong current of carbonic acid is produced, which drives out all the ammonia into the acid; when this strong current ceases somewhat, and before the acid has the opportunity to regurgitate into the hot exhausted tube, the cork is removed, the acid solution emptied into a beaker, the bulbs washed out into the same vessel, the mixture filtered, if necessary, and the excess of

ascertained by titration with normal alkali, as in § 16. Each of acid found to be combined with ammonia represents 0·17 of that substance, or 0·14 grn. of nitrogen.

2. Raw Phosphates and Phosphatic Manures.

oisture and fixed constituents are determined as in the case of no.

00 grains of the manure are lixiviated repeatedly with cold water, he aid of a mortar and pestle, pouring off each washing into aker, allowed to settle, the clear liquid passed through a filter, residue boiled once or twice with water, the fluid being decanted ugh the same filter, the residue is then mainly brought upon it well washed with boiling water; the filtrate and washings so ined are diluted to 500 dm., set aside and marked "Aqueous tion, 100 grn. manure."

he insoluble residue on the filter is pushed through the funnel the beaker in which it was originally digested, the filter treated warm dilute hydrochloric acid, washed with boiling water into beaker, a good quantity of hydrochloric acid added, and the le digested for some time at near boiling heat. The clear acid l is then passed through a filter, the insoluble residue brought n it and washed till all soluble matter is removed, the filtrate washings then diluted to 500 dm., set aside and marked cid solution, 100 grn. manure."

he insoluble residue on the filter is dried, ignited, and weighed, and, clay, &c.

ime and Alkalies, in the aqueous solution, are determined as he case of guano.

ulphuric Acid as in § 40.

hosphoric Acid as in § 69.

n the acid solution, which contains traces of iron, and probably nina, the phosphoric acid is separated and estimated as recomded in § 69. ε.

ime and Sulphuric Acid as in the aqueous solution.

erric Oxide, if necessary, by bichromate or permanganate.

mmonia and Nitrogen as in guano, should the quantity be siderable; if not, a very convenient use may be made of ssler's solution for estimating approximately the ammonia ly formed in the manure, as follows:—1 gm. of the manure is e distilled with 150 c.c. of water and 50 c.c. of solution of sodic carbonate (normal or about that strength) from a small reto arranged as for estimation of ammonia in water § 77. 3; b distilling 50 c.c., the whole of the ammonia will be containe therein, should there be not more than 1% in the manure; b diluting this 50 c.c. of distillate to 500 c.c., and taking 100 c. (= 0·20 gm. of manure) for comparison with standard ammon chloride by Nessler's test, a very near approximation may be obtained.

If the percentage of ammonia is greater than here mentioned, *it* will be preferable to distil into normal acid, as in § 17.

Special procedure for Phosphoric Acid.

In the following processes the estimation of phosphoric acid is in all cases accomplished by means of uranium, as more fully described in § 69. Those who will take the pains to work out the details attentively will find the results very reliable.

Repeated trials side by side with the gravimetric estimation of P^2O^5, as molybdic phosphate and ammonio-magnesic phosphate, have shown the most concordant results in the hands of many well-known and expert operators, among which are Fresenius, Neubauer, Stohmann, Grœser, Kissel, &c. The chief difficulty, as applied to manures of all classes, is the separation of the phosphoric acid in such a form as to be readily and accurately estimated by the process.

In all cases it is advisable to use a solution of uranic acetate or nitrate of such strength, that 1 c.c. or 1 dm. (according to the system of measures used) shall equal 1 per cent. of tricalcic phosphate when 1 gm. or 10 grains respectively of the original substance is taken for analysis. By this arrangement all calculation is avoided. See page 231.

Fresenius, Neubauer, and Luck's Method of examining Phosphatic Substances.

Drs. Fresenius, Neubauer, and Luck, have contributed to Fresenius' Zeitschrift (vol. x. page 133), a method of analysing commercial phosphates, either in the raw or manufactured state, the end in view being to render the operation as speedy as possible, without the sacrifice of accuracy. The condensed results are as follows:—

The experiments made were mostly upon raw phosphates, conaining iron and alumina, such as phosphorite from the Lahn Valley, and upon manufactured phosphates from the same source. These are, as is well known, peculiarly liable to lose soluble phosphate by keeping, and to contain the so-called reduced phosphates.

In the Raw Mineral it is necessary to estimate the total phosphoric acid.

In the Manufactured Manure. 1. The phosphoric acid soluble in cold water = a.

2. The reduced phosphoric acid = b.

3. The insoluble phosphoric acid = c.

From these data is obtained the total phosphoric acid = S.

Estimation of the total Phosphoric Acid in the Raw Mineral.

5 gm. of the finely-powdered phosphates are weighed, transferred o a porcelain mortar, and repeatedly rubbed with about 10 c.c. of a 5 per cent. solution of sulphuric acid, as described at page 239. 10 c.c. of the cold dilute acid are to be used, the creamy mixture is ransferred to a 250 c.c. flask, and the mortar repeatedly washed ut with small portions of water until about 200 c.c. are contained n the flask. The mixture is shaken frequently during about four ours, then diluted to exactly 250 c.c. with water, and well mixed. A dry filter and a dry flask are then got ready, and the liquid iltered; then 100 c.c. transferred to a 200 c.c. flask, rendered listinctly alkaline with caustic soda solution (to neutralize the ulphuric acid), and acetic acid added in sufficient quantity to edissolve the precipitated calcic phosphate. A cloudiness will lways, however, be present if the raw substance contains iron. The whole is diluted to 200 c.c. and set aside in order that the loudiness may deposit. This deposit will consist almost entirely of ferric phosphate, and should be filtered off through a small dry ilter, the filtrate being received into a dry flask, which is corked nd set aside for titration with uranium, and marked *half-strength solution.* The ferric phosphate in the filter is washed repeatedly with small quantities of water (the washings being thrown away), nd finally weighed as ferric phosphate.

The object of using sulphuric acid instead of nitric or hydrochloric, is that of preventing the solution of any large quantity of iron or alumina. Small quantities of these, more especially of iron, will find their way into the solution. The proportion dissolved seems very constant, however; and after using the process a few times, any intelligent operator will judge if any great variation occurs.

The authors here alluded to found that in the special phosphate under examination, containing 32% P^2O^5 = 70% tricalcic phosphate, the amount of P^2O^5 to allow for in the form of ferric phosphate was 2 per cent. This was in a sample containing a considerable quantity of iron. It is probable that wherever there is sufficient iron present to withdraw this quantity of P^2O^5, this proportion of precipitate will occur whatever may be the percentage of tricalcic phosphate. The authors do not recommend that any average allowance should be made for it; but that it should be weighed. My experience, however, goes to prove that where the extraction with cold dilute sulphuric acid has been properly conducted, and where it is not necessary to be absolutely accurate, the trouble of igniting and weighing the precipitate may be avoided, the error in any case being a mere fraction.

Thus far the process is very much like the one described at page 239; but a change is made in the method of titration. It is known that when a solution of phosphate, prepared as above, even with the addition of a little citric acid, is heated (after the ferric phosphate is removed), a precipitate occurs, and most operators have supposed this to be ferric phosphate. It is not so, however, but mainly calcic phosphate; and thus when such a solution is titrated with uranium, the results are too low. In order to avoid this, the process of titration is reversed, *i.e.*, instead of heating the phosphate solution and running the uranium into it, the uranium solution is heated, and the phosphate run into it until no chocolate colour or only a faint one is produced, when the solution is brought in contact with a little powdered potassic ferrocyanide on a white slab.

The authors recommend a solution of uranic acetate, which should be titrated by means of a standard solution of sodic phosphate. 25 c.c. of the uranic solution are placed in a beaker, together with 5 c.c. of sodic acetate solution and 3 c.c. of acetic acid, then heated in a boiling-water bath, and the sodic phosphate solution delivered in from the burette until a drop of the solution brought in contact with the prussiate, just ceases to give a brown colour. Practice will soon enable an operator to understand how much phosphate solution may be run into the uranium before beginning to test, the yellow colour of the latter disappearing as the operation proceeds.

Having by this means established the strength of the uranium solution, the half-strength solution of raw phosphate can now be examined as follows:—25 c.c. of uranium solution are placed in a beaker in the water bath, 5 c.c. of sodic acetate added, and the phosphate solution added from the burette as just described. The quantity of phosphate solution is divided by 2 to obtain the measure of original solution which corresponds to the 25 c.c. of uranium.

The phosphoric acid so found, added to that contained in the ferric phosphate, will of course be the total quantity of P^2O^5 existing in the raw material.

Where 5 gm. of phosphate are dissolved in only 250 c.c. of acid, it is necessary to make a correction for the space occupied in the flask by the calcic sulphate produced and the insoluble matter; experience has proved this to be in the case of 70% phosphate about 0·35% P^2O^5, consequently this must be deducted from the total found as above. Correction may be quite avoided by using a flask of 253 c.c. instead of 250 c.c.; this is, of course, easily done by measuring 3 c.c. into a full 250 c.c. flask, and marking the height of the liquid with a diamond or file. The authors found by this modification of the uranium process the following comparative results:—

	Uranic Method, Volumetric.	Molybdic Method, by Weight.
A sample of Phosphorite = P^2O^5, .	21·54	21·50
,, ,, ,, .	32·14	32·00
,, ,, ,, .	32·03	32·00
A Superphosphate gave soluble P^2O^5,	14·45	14·29
,, ,, another sample,	13·54	13·40

Examination of a Superphosphate.

1. **Soluble Phosphoric Acid.** The manure is exhausted with cold water precisely as described in § 69, p. 231, the flask, however, being well shaken for four hours, then set aside to settle, or a portion filtered for titration. This latter is to be performed precisely as just described for the raw phosphate.

2. **Reduced Phosphoric Acid.** This may be estimated either directly or indirectly. The authors experimented upon the various methods proposed for this form of P^2O^5, such as sodic bicarbonate and ammonic oxalate, neither of which proved satisfactory, the ammonic oxalate process they found, like myself, to be extremely fallacious. The preference is given by them to slightly alkaline ammonic citrate as a means of bringing back the reduced P^2O^5 to the soluble form. The citrate solution should possess a specific gravity of 1·090. By the direct method the residue from 2 gm. of manure, after exhaustion with cold water as above, is washed out of the filter into a mortar by the help of 100 c.c. of citrate solution, and rubbed to a smooth cream, transferred to a flask and digested for half an hour at a temperature of 30° to 40° C.; filtered, washed with some water and citrate solution, and

the filtrate evaporated in a platinum capsule to dryness, ignited with sodic carbonate and potassic nitrate, then extracted with a little dilute sulphuric acid, and titrated with uranium as previously described.

This process is, however, very troublesome, and takes a long time; the indirect method is therefore to be preferred, and the operation conducted as follows:—

Two portions of the manure, weighing 2 gm. each, are respectively exhausted with cold water until the washings are no longer acid. In one of the residues the reduced, and the insoluble P^2O^5 $(b+c)$ are estimated together by the uranium method—50 c.c. of 5 per cent. sulphuric acid being used to dissolve them, as in the case of the raw phosphate, by rubbing in a mortar.

The other residue of 2 gm. is rubbed with 100 c.c. of ammonic citrate solution, and digested as described for the direct process, the filtrate and washings being thrown away; the residue so obtained will consist only of the insoluble phosphate *c.*; the filter is dried, ignited, adding finally a little sodic carbonate, then dissolved with 50 c.c. of dilute sulphuric acid and titrated with uranium as before.

By this means is obtained the insoluble phosphate $= c$ which, subtracted from the previously estimated mixture of the reduced and insoluble $P^2O^5 = (b+c)$, will give the quantity of reduced $P^2O^5 = b$.

Thus are furnished the data from which may be calculated the total percentage of P^2O^5 in the manure by the equation,

$$S = a + b + c \text{ whence } (a + b) = S - c.$$

It is not possible to estimate the amount of soluble and reduced phosphoric acid in one operation, because when neutral ammonic citrate is mixed with acid calcic phosphate, it gives rise to acid ammonic citrate, which would have much more disintegrating power over the insoluble phosphate than the neutral or faintly alkaline solution.

The estimations, therefore, necessary to ascertain the complete character of a superphosphate are:—

The total $P^2O^5 = S$
soluble „ $= a$
insoluble „ $= c$

and from these may be obtained the quantity of reduced P^2O^5, according to the formula

$$b = S - (a + c)$$

As an example, a specimen of superphosphate of a reddish colour, showing the presence of much iron, was analysed and gave the following results:—

1. Total P^2O^5, . . $15{\cdot}80\% = S$
2. Soluble, „ . . $3{\cdot}84\% = a$
3. Insoluble, „ . . $7{\cdot}12\% = c$

Consequently $b = 15{\cdot}80 - (3{\cdot}84 + 7{\cdot}12) = 4{\cdot}84\%$.

ANALYSIS OF NATURAL WATERS AND SEWAGE.

§ 76. THE analysis of natural waters and sewage has for a long period received the attention of chemists, but until lately no methods of examination have been produced which could be said to satisfy the demands of those who have been interested in the subject from various points of view. The researches of Clark, Frankland, Armstrong, Miller, Wanklyn, and others, have, however, now brought the whole subject into a more satisfactory form, so that it may fairly be said that, as regards accuracy of chemical processes, or interpretation of results from a sanitary point of view, very little addition is required. Considerable space will be devoted to the matter here; and as most of the processes are now volumetric and admit of ready and accurate results, the general subject naturally falls within the scope of this work. Considerable pains have been taken to render the treatment of the matter practical and trustworthy.

Since the various processes necessitate the use of peculiar materials and apparatus, the preparation and arrangement of these will be described at some length previous to the introduction of the general subject.

THE PREPARATION OF RE-AGENTS.

A. Re-agents required for the Estimation of Nitrogen present as Ammonia.

a. **Nessler's Solution.** Dissolve 62·5 gm. of potassic iodide in about 250 c.c. of distilled water, set aside a few c.c., and add gradually to the larger part a cold saturated solution of corrosive sublimate until the mercuric iodide precipitated ceases to be redissolved on stirring. When a permanent precipitate is obtained, restore the reserved potassic iodide so as to redissolve it, and continue adding corrosive sublimate very gradually until a slight precipitate remains undissolved. (The small quantity of potassic iodide is set aside merely to enable the mixture to be made rapidly without danger of adding an excess of corrosive sublimate.)

Next dissolve 150 gm. of solid potassic hydrate (that usually sold in sticks or cakes) in 150 c.c. of distilled water, allow the solution to cool, add it gradually to the above solution, and make up with distilled water to one litre.

On standing, a brown precipitate is deposited, and the solution becomes clear, and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle as required.

β. **Standard Solution of Ammonic Chloride.** Dissolve 1·9107 gm. of pure dry ammonic chloride in a litre of distilled water; of this take 100 c.c., and make up to a litre with distilled water. The latter solution will contain ammonic chloride corresponding to 0·00005 gm. of nitrogen in each c.c. In use it should be measured from a narrow burette of 10 c.c. capacity divided into tenths.

[If it is desired to estimate "*ammonia*" rather than "*nitrogen as ammonia*" take 1·5735 gm. of ammonic chloride instead of 1·9107 gm. 1 c.c. will then correspond to 0·00005 gm. of ammonia (NH^3).]

γ. **Sodic Carbonate.** Heat anhydrous sodic carbonate to redness in a platinum crucible for about an hour, taking care not to fuse it. Allow to cool, and whilst still warm rub it in a clean mortar so as to break any lumps which may have been formed, and transfer to a clean dry wide-mouth stoppered bottle. Too large a quantity should not be kept in one bottle, lest by prolonged use ammoniacal impurities get in. A bottle holding about 100 c.c. is a convenient size.

δ. **Water free from Ammonia.** If, when 1 c.c. of Nessler's solution (**A.** *a.*) is added to 100 c.c. of distilled water in a glass cylinder, standing on a white surface (*see* Estimation of Ammonia), no trace of a yellow tint is visible after five minutes, the water is sufficiently pure for use. As, however, this is rarely the case, the following process must usually be adopted. Distil from a large glass retort (or better, from a copper or tin vessel holding 15–20 litres) ordinary distilled water which has been rendered distinctly alkaline by addition of sodic carbonate. A glass Liebig's condenser, or a clean tin worm should be used to condense the vapour; it should be connected to the still by a short india-rubber joint. Test the distillate from time to time with Nessler's solution, as above described, and when free from ammonia collect the remainder for use. The distillation must not be carried to dryness. Ordinary water may be used instead of distilled water, but it occasionally continues for some time to give off traces of ammonia by the slow decomposition of the organic matter present in it.

B. Re-agents required for the Estimation of Organic Carbon and Nitrogen.

α. Water free from Ammonia and Organic Matter. Distilled water, to which 1 gm. of potassic hydrate and 0·2 gm. of potassic permanganate per litre have been added, is boiled gently for about twenty-four hours in a similar vessel to that used in preparing water free from ammonia (A. δ.), an inverted condenser being so arranged as to return the condensed water. At the end of that time the condenser is adjusted in the usual way, and the water carefully distilled, the distillate being tested at intervals for ammonia, as in preparing A. δ. When ammonia is no longer found, the remainder of the distillate may be collected, taking care to stop short of dryness. The neck of the retort or still should point slightly upwards, so that the joint which connects it with the condenser is the highest point. Any particles carried up mechanically will then run back to the still, and not contaminate the distillate. The water thus obtained should then be rendered slightly acid with sulphuric acid, and re-distilled from a clean vessel for use, again stopping short of dryness.

β. Solution of Sulphurous Acid. Sulphurous anhydride is prepared by the action of sulphuric acid upon cuttings of metallic copper. The gas is made to bubble through water to remove mechanical impurities, and then conducted into water free from ammonia and organic matter (B. α.) until a saturated solution is obtained.

γ. Solution of Hydric Sodic Sulphite. Sulphurous anhydride, prepared and washed as above, is passed into a solution of sodic carbonate made by dissolving ignited sodic carbonate (A. γ.) in water free from ammonia and organic matter (B. α.). The gas is passed until carbonic anhydride ceases to be evolved.

δ. Solution of Ferrous Chloride. Pure crystallized ferrous sulphate is dissolved in water, precipitated by sodic hydrate, the precipitate well washed (using pure water B. α. for the last washings), and dissolved in the smallest possible quantity of pure hydrochloric acid. Two or three drops must not contain an appreciable quantity of ammonia. It is convenient to keep the solution in a bottle with a ground glass cap instead of a stopper, so that a small dropping tube may be kept in it always ready for use.

ε. Cupric Oxide is prepared by heating to redness with free access of air, on the hearth of a reverberatory furnace, or in a muffle, copper wire cut into short pieces, or copper sheets cut into strips. That which has been made by calcining the nitrate cannot be used, as it appears to be impossible to expel the last traces of nitrogen. After use, the oxide should be extracted by breaking the combustion tube, rejecting the portion which was mixed with the substance examined. As soon as a sufficient quantity has been recovered, it should be recalcined. This is most conveniently done in an iron tube about 30 m.m. in internal diameter, and about the same length as the combustion furnace. One end should be closed with a cork, the cupric oxide poured in, the tube placed in the combustion furnace (which is tilted at an angle of about 15°, so as to produce a current of air), the cork removed, and the tube kept at a red heat for about two hours. In a Hofmann's gas furnace, with five rows of burners, two such tubes may be heated at the same time if long clay burners are placed in the outer rows, and short ones in the three inner rows. If the furnace has but three rows of burners, a rather smaller iron tube must be used. When cold, the oxide can easily be extracted, if the heat has not been excessive, by means of a stout iron wire, and should be kept in a clean dry stoppered bottle. Each parcel thus calcined should invariably be assayed by filling with it a combustion tube of the usual size, and treating it in every respect as an ordinary combustion. It should yield only a very minute bubble of gas, which should be almost wholly absorbed by potassic hydrate. (The quantity of CO^2 found should not correspond to more than 0·00005 gm. of C.) The finer portions of the oxide should, after calcining, be sifted out by means of a sieve of clean copper gauze, and reserved for use as described hereafter.

New cupric oxide as obtained from the reverberatory furnace should be assayed, and if not sufficiently pure, as is most likely the case, calcined as above described, and assayed again.

ζ. **Metallic Copper.** Fine copper gauze is cut into strips about 80 m.m. wide, and rolled up as tightly as possible on a copper wire so as to form a compact cylinder 80 m.m. long. This is next covered with a tight case of moderately thin sheet copper, the edges of which meet without overlapping. The length of the strip of gauze, and the consequent diameter of the cylinder, must be regulated so that it will fit easily, but not too loosely in the combustion tubes. A sufficient number of these cylinders being prepared, a piece of combustion tube is filled with them, and they are heated to redness in the furnace, a current of atmospheric air being passed through them for a few minutes in order to burn off organic impurity, and coat the copper gauze superficially with oxide. A current of hydrogen, dried by passing through strong sulphuric acid, is then substituted for the air, and a red heat maintained until hydrogen issues freely from the end of the tube. It is then allowed to cool, the current of hydrogen being continued, and when cold the copper cylinders are removed and kept in a stoppered bottle. After each time of using they must be heated in a stream of hydrogen as before, and are then again ready for use. The heating in air need not be repeated.

η. **Solution of Potassic Bichromate** is used as a test for and to absorb sulphurous anhydride which may be present in the gas obtained by combustion of the water residue. It should be saturated, and does not require any special attention. The yellow neutral chromate may also be used, but must be rendered slightly acid, lest it should absorb carbonic as well as sulphurous anhydride.

θ. **Solution of Potassic Hydrate.** A cold saturated solution made by dissolving solid potassic hydrate in distilled water.

ι. **Solution of Pyrogallic Acid.** A cold saturated solution, made by dissolving in distilled water solid pyrogallic acid obtained by sublimation.

κ. **Solution of Cuprous Chloride.** A saturated solution of cupric chloride is rendered strongly acid with hydrochloric acid, a quantity of metallic copper introduced in the form of wire or turnings, and the whole allowed to stand in a closely stoppered bottle until the solution becomes colourless.

λ. **Oxygen.** Blow a bulb of about 30 c.c. capacity at the end of a piece of combustion tube, and draw out the tube so that its internal diameter for a length of about 300 m.m. is about 3 m.m. This is done in order that the capacity of the apparatus apart from the bulb may be as small as possible. Cut the tube at the wide part about 10 m.m. from the point at which the narrow tube commences, thus leaving a small funnel-shaped mouth. Then introduce, a little at a time, dried, coarsely powdered, potassic chlorate until the bulb is full. Cut off the funnel, and, at a distance of 100 m.m. from the bulb, bend the tube at an angle of 45°, and at 10 m.m. from the end bend it at right angles in the opposite direction. It then forms a retort and delivery tube in one piece, and must be adjusted in a mercury trough in the usual manner, taking care that the end does not dip deeper than about 20 m.m. below the surface, as otherwise the pressure of so great a column of mercury might destroy the bulb when softened by heat. On gently heating, the potassic chlorate fuses and evolves oxygen. The escaping gas is collected in test tubes about 150 m.m. long and 20 m.m. in diameter, rejecting the first 60 or 80 c.c., which contain the nitrogen of the air originally in the bulb retort. Five or more of these tubes, according to the quantity of oxygen required, are collected and removed from the mercury trough, in very small beakers, the mercury in which should be about 10 m.m. above the end of the test tube. Oxygen may be kept in this way for any desired length of time, care being taken, if the temperature falls considerably, that there is sufficient mercury in the beaker to keep the mouth of the test tube covered. About 10 c.c. of the gas in the first tube collected is transferred by decantation in a mercury trough to another tube, and treated with potassic hydrate and pyrogallic acid, when, if after a few minutes it is absorbed with the exception of a very small bubble, the gas in that and the remaining tubes may be considered pure. If not, the first tube is rejected and the second tested in the same way, and so on.

μ. **Hydric Metaphosphate.** The glacial hydric metaphosphate, usually sold in sticks, is generally free from ammonia, or very nearly so. A solution should be made containing about 100 gm. in a litre. It should be so far free from ammonia as that 10 c.c. do not contain an appreciable quantity.

ν. **Calcic Phosphate.** Prepared by precipitating common hydric disodic phosphate with calcic chloride, washing the precipitate with water by decantation, drying, and heating to redness for an hour.

C. Re-agents required for the Estimation of Nitrogen present as Nitrates and Nitrites.

a. **Solution of Argentic Sulphate.** Argentic carbonate is precipitated from the nitrate by sodic carbonate, washed well by decantation, and converted into sulphate by the addition of hydric sulphate in slight excess; the excess of acid is carefully neutralized with potassic hydrate, and the sparingly soluble argentic sulphate washed with cold water by decantation until 100 c.c. evaporated to dryness and tested as hereafter described (§ 77. 6) are found to contain no nitrate. It should be kept in a rather large bottle filled up with distilled water, and the clear saturated solution of argentic sulphate decanted into a smaller bottle as required for use. The large bottle is replenished with water from time to time, being well shaken on each addition, until the whole of the sulphate is consumed.

β. **Concentrated Sulphuric Acid.** The ordinary colourless acid is usually free from nitrates and nitrites. It should be tested before use by the method described hereafter for the estimation of nitrogen as nitrates. (§ 77. 6)

γ. **Potassic Permanganate.** Dissolve about 10 gm. of crystallized potassic permanganate in a litre of distilled water.

δ. **Sodic Carbonate.** Dissolve about 10 gm. of dry, or an equivalent quantity of crystallized sodic carbonate free from nitrates, in a litre of distilled water.

For the Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, but little Organic Nitrogen.

ε. **Metallic Aluminium.** As thin foil.

ζ. **Solution of Sodic Hydrate.** Dissolve 100 gm. of solid sodic hydrate in a litre of distilled water; when cold, put it in a tall glass cylinder, and introduce about 100 sq. cm. of aluminium foil, which must be kept at the bottom of the solution by means of a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about one-third of its volume has been evaporated, allow to cool, and make up to its original volume with water free from ammonia. The absence of nitrates is thus ensured.

η. **Broken Pumice.** Clean pumice is broken in pieces of the size of small peas, sifted free from dust, heated to redness for about an hour, and kept in a closely stoppered bottle.

θ. **Hydrochloric Acid free from Ammonia.** If the ordinary pure acid is not free from ammonia, it should be rectified from sulphuric acid. As only two or three drops are used in each experiment, it will be sufficient if that quantity does not contain an appreciable proportion of ammonia.

For the Estimation of Nitrogen as Nitrates and Nitrites by the Indigo Process.

ι. **Standard Solution of Potassic Nitrate.** The standard solution described on p. 112, (1·011 gm. of KNO^3 per litre) may be used, but a weaker solution is more convenient for water analysis. A useful strength is 0·02 gm. of nitrogen, or 0·14442 gm. of KNO_3 per litre.

κ. **Standard Solution of Indigo.** The solution described on p. 112 may be used, but a weaker one is more convenient. A strength such that 10 c.c. are discolorized by 10 c.c. of the nitrate (C. ι.) is very useful. It should be prepared and its exact strength ascertained as described on p. 112.

λ **Concentrated Sulphuric Acid.** This must have a sp. gr. not less than 1·8, must not become turbid on dilution with water, and must of course be free from nitrous compounds.

D. Re-agents required for the Estimation of Chlorine present as Chloride.

α. **Standard Solution of Argentic Nitrate.** Dissolve 2·3944 gm. of pure recrystallized argentic nitrate in distilled water, and make up to a litre. In use it is convenient to measure it from a burette which holds 10 c.c. and is divided into tenths.

β. **Solution of Potassic Chromate.** A strong solution of pure neutral potassic chromate free from chlorine. It is most conveniently kept in a bottle similar to that used for the solution of ferrous chloride. (B. δ.)

E. Re-agents required for determination of Hardness.

α. **Standard Solution of Calcic Chloride.** Dissolve in dilute hydric chloride, in a platinum dish, 0·2 gm. of pure crystallized calcite, adding the acid gradually, and having the dish covered with a glass plate, to prevent loss by spirting. When all is dissolved, evaporate to dryness on a water bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of hydric chloride. Lastly, dissolve the calcic chloride in distilled water, and make up to one litre.

β. **Standard Solution of Potassic Soap.** Rub together in a mortar 150 parts of lead plaster (Emplast. Plumbi of the druggists) and 40 parts of dry potassic carbonate. When they are fairly mixed, add a little methylated spirit and continue triturating until a uniform creamy mixture is obtained. Allow to stand for some hours, then throw on to a filter and wash several times with methylated spirit. The strong solution of soap thus obtained must be diluted with a mixture of one volume of distilled water and two volumes of methylated spirit (considering the soap solution as spirit), until exactly 14·25 c.c. are required to form a permanent lather with 50 c.c. of the standard calcic chloride (E. *a*.) the experiment being performed precisely as in determining the hardness of a water. A preliminary assay should be made with a small quantity of the strong soap solution to ascertain its strength. It is better to make the solution a little too strong at first, and dilute it to the exact strength required, as it is easier to add alcohol accurately than strong soap solution. After making the solution approximately of the right strength, allow it to stand twenty-four hours; and then, if necessary, filter it, and afterwards adjust its strength accurately.

ANALYTICAL PROCESSES.

§ 77. To form for sanitary purposes, an opinion of the character of a natural water or sewage, it will in most cases suffice to determine the nitrogen as ammonia, organic carbon, organic nitrogen, total solid matter, nitrogen as nitrates and nitrites, suspended matter, chlorine, and hardness, and in the following pages the estimation of these will be considered in detail, and then more briefly that of other impurities.

The method of estimating nitrogen as ammonia is substantially that described by the late Dr. W. A. Miller in the Journal of the Chemical Society, ser. ii., vol. 3, p. 125; and that for estimating organic carbon and nitrogen, was devised by Drs. Frankland and Armstrong, and described by them in the same journal, ser. ii., vol. 6, p. 77 *et seq.*

1. Collection of Samples.

The points to be considered under this head are the vessel to be used, the quantity of water required, and the method of ensuring a truly representative sample.

Stoneware bottles should be avoided, as they are apt to affect the hardness of the water, and are more difficult to clean than glass. Stoppered glass bottles should be used if possible; those known as "Winchester Quarts," which hold about two-and-a-half litres each, are very convenient and easy to procure. One of these will contain sufficient for the general analysis of sewage and largel polluted rivers, two for well waters and ordinary rivers and stream and three for lakes and mountain springs. If a more detaile analysis is required, of course a larger quantity must be taken.

If corks must be used, they should be *new*, and well washe with the water at the time of collection.

In collecting from a well, river, or tank, plunge the bottle itsel if possible, below the surface; but if an intermediate vessel mu be used, see that it is thoroughly clean and well rinsed with th water. Avoid the surface water and also any deposit at th bottom.

If the sample is taken from a pump or tap, take care to let th water which has been standing in the pump or pipe run off befo collecting, then allow the stream to flow directly into the bottl If it is to represent a town water supply, take it from the servic pipe communicating directly with the street main, and not from cistern.

In every case, first fill the bottle completely with the wate empty it again, rinse once or twice carefully with the water, an then fill it nearly to the stopper, and tie down tightly.

At the time of collection note the source of the sample, wheth from a deep or shallow well, a river, or spring, and also its loc name so that it may be clearly identified.

If it is from a well, ascertain the nature of the soil, subsoil, an water-bearing stratum, the depth and diameter of the well, i distance from neighbouring cesspools, drains, or other sources pollution; whether it passes through an impervious stratum befo entering the water-bearing stratum, and if so, whether the sides the well above this are, or are not, water-tight.

If the sample is from a river, ascertain the distance from t source to the point of collection; whether any pollution tak place above that point, and the geological nature of the distri through which it flows.

If it is from a spring, take note of the stratum from which issues.

2. Preliminary Observations.

In order to insure uniformity, the bottle should invariably well shaken before taking out a portion of the sample for a purpose. The *colour* should be observed as seen in a tall, narro cylinder standing upon a white surface. It is well to compare it with distilled water in a similar vessel. The *taste* and *odour* are most easily detected when the water is heated to 30°— 35° C.

Before commencing the quantitative analysis, it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. As a general rule, if the suspended matter is to be determined, the water should be filtered before the estimation of organic carbon and nitrogen, nitrogen as ammonia, and total solid residue; if otherwise, it should merely be shaken up. If the suspended matter is *not* determined, the appearance of the water, as whether it is clear or turbid, should be noted. This is conveniently done when measuring out the quantity to be used for the estimation of organic carbon and nitrogen. If the measuring flask be held between the eye and a good source of light, but with an opaque object, such as a window bar, in the line drawn from the eye through the centre of the flask, any suspended particles will be seen well illuminated on a dark ground.

Water derived from a newly sunk well, or which has been rendered turbid by the introduction of innocuous mineral matter from some temporary and exceptional cause should be filtered, but the suspended matter, in most cases, need not be determined. The introduction of organic matter of any kind would almost always render the sample useless.

3. Estimation of Nitrogen as Ammonia.

Place about 50 c.c. of the water in a glass cylinder about 150 m.m. high, and of about 70 c.c. capacity, standing upon a white glazed tile or white paper. Add about 1 c.c. of Nessler's solution (A. α.), stir with a clean glass rod, and allow to stand for a minute or so. If the colour then seen does not exceed in intensity that produced when 0·1 c.c. of the standard ammonic chloride (A. β.) is added to 50 c.c. of water free from ammonia (A. δ.), and treated in the same way, half a litre of the water should be used for the estimation. If the colour be darker, a proportionately smaller quantity should be taken, but it is not convenient to use less than 20 or 25 c.c.

If it has been decided that the water should be filtered before analysis, care must be taken, should it contain only a small quantity of ammonia, that the *filter paper* is free from ammonia. If it is not, it must be steeped in water free from ammonia for a day or so, and when used, the first portion of the filtrate rejected. *Washing* with water, even if many times repeated, is generally ineffectual. When a large quantity of ammonia is present, as in highly polluted water and sewage, any ammonia in the filter paper may be neglected. A moderate quantity of suspended matter may also generally be neglected with safety, even if the water is to be filtered in estimating organic carbon and nitrogen and total solid matter.

The water, filtered or unfiltered as the case may be, should be carefully measured and introduced into a capacious retort, connected by an india-rubber joint with a Liebig's condenser, the volume being, if necessary, made up to about 400 c.c. with water free from ammonia. Add about 1 gm. of sodic carbonate (A. γ.), and distil rapidly, applying the lamp flame directly to the retort, and collect the distillate in a small glass cylinder, such as is described above. When about 50 c.c. have distilled into the first cylinder, put it aside and collect a second 50 c.c., and as soon as that is over remove the lamp, and add to the *second* distillate about 1 c.c. of Nessler's solution, stir with a clean glass rod, and allow to stand on a white tile or sheet of paper for five minutes. To estimate the ammonia present, measure into a similar cylinder as much of the standard ammonic chloride solution as you judge by the colour to be present in the distillate, make it up with water free from ammonia to the same volume, and treat with Nessler's solution in precisely the same way. If, on standing, the intensity of colour in the two cylinders is equal, the quantity of ammonia is also equal, and this is *known* in the trial cylinder. If it is not equal, another trial must be made with a greater or less quantity of ammonic chloride. The ammonic chloride must not be added *after* the Nessler's solution, or a turbidity will be produced which entirely prevents accurate comparison. If the ammonia in the second distillate does not exceed that in 0·2 c.c. of the standard ammonic chloride, the distillation need not be proceeded with any farther, but if otherwise, successive quantities must be distilled and tested until ammonia ceases to be found. If the ammonia in the second distillate corresponds to 0·4 c.c. or less of the ammonic chloride, that in the first may be estimated in the same way, but if the second contains a greater quantity of ammonia, the first must be measured, and an aliquot part taken and diluted to about 50 c.c. with water free from ammonia, as it is likely to contain so much ammonia as to give a colour too intense to admit of easy comparison. A colour produced by more than 2 c.c. of ammonic chloride cannot be conveniently employed. When, as in the case of sewage, a large quantity of ammonia is known to be present, it saves trouble to distil about 100 c.c. at first, and at once take an aliquot part of that as above described. If the liquid spirts in distilling, arrange the retort so that the joint between the retort and condenser is the highest point; the distillation will proceed rather more slowly, but anything carried up mechanically will be returned to the retort. When the ammonia has been estimated in all the distillates, add together the corresponding volumes of ammonic chloride solution; then, if 500 c.c. have been employed for the experiment, the number of c.c. of ammonic chloride used divided by 100 will give the quantity of nitrogen as ammonia in 100,000 pts. of the water; if less than that, say y c.c. have been used, multiply the volume of ammonic chloride by $\frac{500}{y}$ and divide by 100 as before.

Before commencing this operation, ascertain that the retort and condenser are free from ammonia by distilling a little common water or distilled water with sodic carbonate until the distillate is free from ammonia. Remove the residue then, and after each estimation, by means of a syphon, without disconnecting the retort. If a small quantity of water is to be distilled, the residue or part of it from a previous experiment may be left in the retort, instead of adding water free from ammonia, care being taken that the previous distillation was continued until ammonia ceased to be evolved.

When urea is present the evolution of ammonia is long continued, owing to the decomposition of the urea; in such cases collect the distillate in smaller quantities, and as soon as the first rapid diminution in the amount of ammonia has ceased, neglect the remainder, as this would be due almost wholly to decomposition of the urea.

4. Estimation of Organic Carbon and Nitrogen.

This should be commenced as soon as the nitrogen as ammonia has been determined. If that is less than 0·05 part per 100,000, a litre should be used; if more than 0·05, and less than 0·2, half a litre; if more than 0·2, and less than 1·0, a quarter of a litre; if more than 1·0, a hundred c.c. or less. These quantities are given as a guide in dealing with ordinary waters and sewage, but subject to variation in exceptional cases. A quantity which is too large should be avoided as entailing needless trouble in evaporation, and an inconveniently bulky residue and resulting gas. If it is to be filtered before analysis, the same precaution as to filter paper must be taken as for estimation of nitrogen as ammonia, the same filter being generally used.

Having measured the quantity to be used, add to it in a capacious flask 15 c.c. of the solution of sulphurous acid (B. β.), and boil briskly for a few seconds, in order to decompose the carbonates present. Evaporate to dryness in a hemispherical glass dish, about a decimetre in diameter, and preferably without a lip, supported in a copper dish with a flange (fig. 34, *d e*). The flange has a diameter of about 14 centimetres, is sloped slightly towards the centre, and has a rim of about 5 m.m. turned up on its edge, except at one point, where a small lip is provided. The concave portion is made to fit the contour of the outside of the glass dishes, and is of such a depth as to allow the edge of the dish to rise about 15 m.m. above the flange. The diameter of the concavity at *f* is about 90 m.m., and the depth at *g* about 30 m.m. A thin glass shade, such as is used to protect statuettes, about 30 centimetres high, stands on the flange of the copper dish, its diameter being such as to fit without difficulty on the flange, and leave a sufficient space between its interior surface and the edge of the glass dish. The copper dish is supported on a steam or water bath, and the water as it evaporates is condensed on the interior of the glass shade, runs down into the copper dish, filling the space between it and the glass dish, and then passes off by the lip at the edge of the flange, a piece of tape held by the edge of the glass shade, and hanging over the lip, guiding it into a vessel placed to receive it.

We are indebted to Mr. Bischof for an improved apparatus for evaporation, which by keeping the dish always full by a self-acting contrivance, permits the operation to proceed without attention during the night, and thus greatly reduces the time required. This form of apparatus is shown in fig. 34. The glass dish *d* is supported by a copper dish *e* as described above, and resting on the latter is a stout copper ring *h* which is slightly conical, being 115 m.m. in diameter at the top and 130 at the bottom. At the top is a narrow flange of about 10 m.m. with a vertical rim of about 5 m.m. The diameter across this flange is the same as the diameter of the dish *e*, so that the glass shade *i* will fit securely either on *h* or *e*. The height of the conical ring is about 80 m.m.

The automatic supply is accomplished on the well-known principle of the bird fountain, by means of a delivery tube *b*, the upper end of which is enlarged to receive the neck of the flask *a* containing the water to be evaporated, the joint being carefully ground so as to be water-tight. The upper vertical part of *b*, including this enlargement, is about 80 m.m. in length, and the sloping part about 260 m.m. with a diameter of 13 m.m. The lower end which goes into the dish is again vertical for about 85 m.m., and carries a side tube *c* of about 3 m.m. internal diameter, by which air enters the delivery tube whenever the level of the water in the dish falls below the point at which the side tube joins the delivery tube. The distance from this point to the end of the tube which rests on the bottom of the dish at *g*, and is there somewhat con-

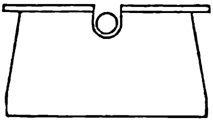

Fig. 35.

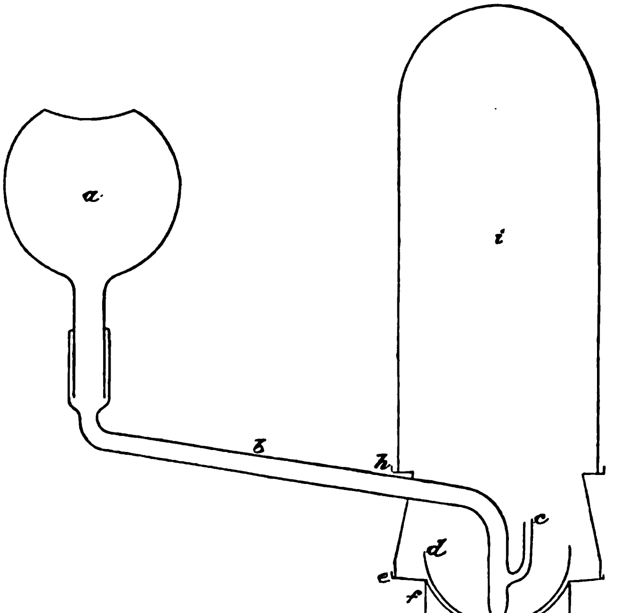

Fig. 34.

stricted, is about 30 m.m. The side tube *c* should not be attached on the side next the flask, as if so the inclined part of *b* passes over its mouth and renders it very difficult to clean. The flask *a* should hold about 1200 c.c., and have a rather narrow neck—about 20 m.m.—and a flat bottom. A small slot is cut in the upper edge of the copper ring *h* to accommodate the delivery tube, as shown in fig. 35. Its size and shape should be such that the tube does not touch the edge of the glass shade *i*, lest water running down the inner surface of the shade should find its way down the outside of the delivery tube into the dish. This being avoided, the opening should be as closely adjusted to the size of the delivery tube as can be. The copper dish *e* should rest on a steam or water bath, so that only the spherical part is exposed to the heat.

After the addition of the 15 c.c. of sulphurous acid, the water may either be boiled in the flask *a*, or in another more capacious one, and then transferred to *a*. It should be allowed to cool before the delivery tube is adjusted, otherwise the joint between the two is liable to become loose by expansion of the delivery tube.

The glass dish having been placed on the copper dish *e*, the conical ring *h* is fitted on, and the flask with the delivery tube attached inverted, as shown in fig. 34, *a*, *b*. This should not be done too hurriedly, and with a little care there is no risk of loss. The flask is supported either by a large wooden filtering stand, the ring of which has had a slot cut in it to allow the neck of the flask to pass, or by a clamp applied to the upper end of the delivery tube where the neck of the flask fits in. The delivery tube having been placed in the slot made to receive it, the glass shade is fitted on, and the evaporation allowed to proceed. When all the water has passed from the flask into the dish, the flask and delivery tube, and the conical ring *h* may be removed, and the glass shade placed directly on the dish *e* until the evaporation is complete. If the water is expected to contain a large quantity of nitrates, two or three drops of chloride of iron (B. δ.) should be added to the first dishful; and if it contains little or no carbonate, one or two c.c. of hydric sodic sulphite (B. γ.). The former facilitates the destruction of nitrates and nitrites, and the latter furnishes base for the sulphuric acid produced by oxidation of the sulphurous acid, and which would, if free, decompose the organic matter when concentrated by evaporation. An estimate of the quantity of carbonate present, sufficiently accurate for this purpose, may generally be made by observing the quantity of precipitate thrown down on addition of sodic carbonate in the determination of nitrogen as ammonia.

With sewages and very impure waters (containing upwards of 0·1 part of nitrogen as ammonia per 100,000 for example) such great precaution is hardly necessary, and the quantity to evaporate being mall, the evaporation may be conducted in a glass dish placed irectly over a steam bath, and covered with a drum or disc of filter aper made by stretching the paper by means of two hoops of light plit cane, one thrust into the other, the paper being between them, n the way often employed in making dialysers. This protects the ontents of the dish from dust, and also, to a great extent, from mmonia which may be in the atmosphere, and which would impair he accuracy of the results. As a glass dish would be in some danger f breaking by the introduction of *cold* water, the flask containing he water being evaporated in this or in the first described manner, must be kept on a hot plate or sand bath at a temperature of about 0° or 70° C., and should be covered with a watch glass. This recaution is not necessary when Bischof's apparatus is used. f, at any time, the water in the flask ceases to smell strongly of ulphurous acid, more should be added. The preliminary boiling may be omitted when less than 250 c.c. is used. When the nitrogen as nitrates and nitrites exceeds 0·5 part, the dish, after the evaporation has been carried to dryness, should be filled with distilled water containing ten per cent. of saturated sulphurous acid solution, and the evaporation again carried to dryness; if it exceeds 1·0 part, a quarter of a litre of this solution should be evaporated on the residue; if 2·0 parts, half a litre; and if 5 parts, a litre. If less than a litre has been evaporated, a proportionally smaller volume of this solution may be used. The estimation of nitrogen as nitrates and nitrites will usually be accomplished before this stage of the evaporation is reached.

In the case of sewage, however, it is advisable to employ hydric metaphosphate in the place of sulphurous acid, as the ammonic phosphate is even less volatile than the sulphite. This can only be employed for sewage and similar liquids, which are free from nitrates and nitrites. To the measured quantity of liquid to be evaporated, add, in the glass dish, 10 c.c. of the hydric metaphosphate (B. μ.), and, in order to render the residue more convenient to detach from the dish, about half a gramme of calcic phosphate (B. ν.), and proceed as usual. No chloride of iron, sulphurous acid, or sodic sulphite is required; nor is it necessary to boil before commencing the evaporation.

The next operation is the combustion of the residue. The combustion tube should be of hard, difficultly fusible glass, with an internal diameter of about 10 m.m. Cut it in lengths of about 430 m.m., and heat one end of each in the blowpipe flame to round the edge. Wash well with water, brushing the interior carefully with a tube brush introduced at the end whose edge has been rounded, rinse with distilled water, and dry in an oven. When dry, draw off and close, at the blowpipe, the end whose edge has been left sharp. The tube is then ready for use.

Pour on to the perfectly dry residue in the glass dish, standing on a sheet of white glazed paper, a little of the fine cupric oxide (B. ε.), and with the aid of a small elastic steel spatula (about 100 m.m. long and 15 m.m. wide) carefully detach the residue from the glass and rub it down with the cupric oxide. The spatula readily accommodates itself to the curvature of the dish and effectually scrapes its surface. When the contents of the dish are fairly mixed, fill about 30 m.m. of the length of the combustion tube with granulated cupric oxide (B. ε.), and transfer the mixture in the dish to the tube. This is done in the usual way by a scooping motion of the end of the tube in the dish, the last portions being transferred by the help of a bent card or a piece of clean and smooth platinum foil. Rinse the dish twice with a little fine cupric oxide, rubbing it well round each time with the spatula, and transfer to the tube as before. Any particles scattered on the paper are also to be put in. Fill up to a distance of 270 m.m. from the closed end with granular cupric oxide, put in a cylinder of metallic copper (B. ζ.), and then again 20 m.m of granular cupric oxide. This last is to oxidise any traces of carbonic oxide which might be formed from carbonic anhydride by the reducing action of iron or other impurity in the metallic copper. Now draw out the end of the tube so as to form a neck about 100 m.m. long and 4 m.m. in diameter, fuse the end of this to avoid injury to the india-rubber connector, and bend it at right angles. It is now ready to be placed in the combustion furnace and attached to the Sprengel pump.

The most convenient form of this instrument for the purpose is shown in fig. 36. The glass funnel *a* is kept supplied with mercury, and is connected by a caoutchouc joint with a long narrow glass tube which passes down nearly to the bottom of a wider tube *d*, 900 m.m. long, and 10 m.m. in internal diameter. The upper end of *d* is cemented into the throat of a glass funnel *c* from which the neck has been removed. A screw clamp *b* regulates the flow of mercury down the narrow tube. A piece of ordinary glass tube *f g*,

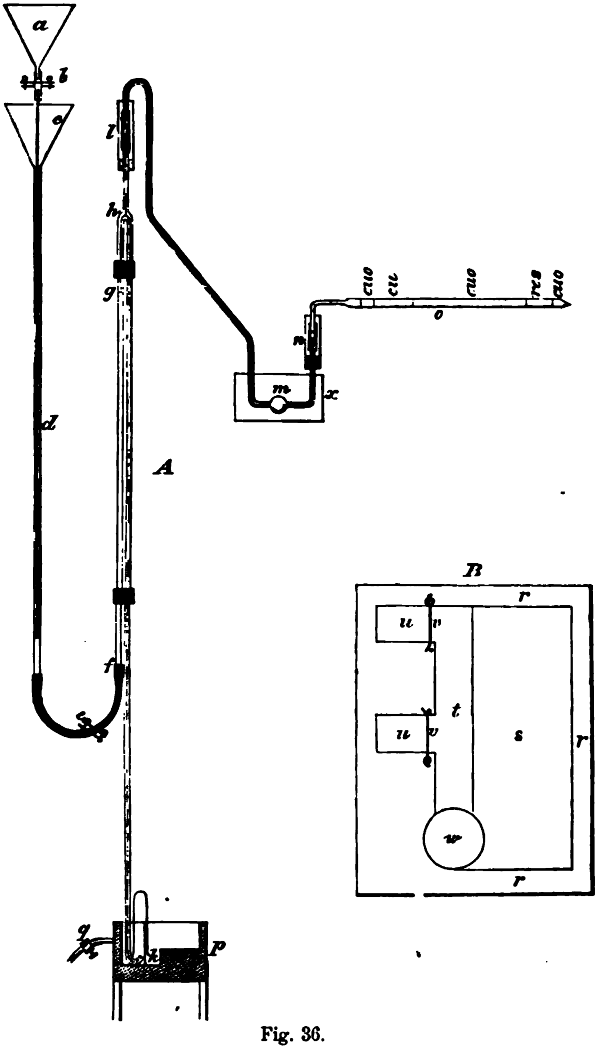

Fig. 36.

about 6 m.m. in diameter and 600 m.m. in length, is attached at *g* to a tube *ghk*, about 6 m.m. in diameter, 1500 m.m. long, with a bore of 1 m.m. This is bent sharply on itself at *h*, the part *hk* being 1300 m.m. long, and the two limbs are firmly lashed together with copper wire at two points, the tubes being preserved from injury by short sheaths of caoutchouc tube. The end *k* is recurved for the delivery of gas. At the top of the bend at *h*, a piece of ordinary tube *h l*, about 120 m.m. long, and 5 m.m. in diameter, is sealed on. The whole *l k* is kept in a vertical position by a loose support or guide, near its upper part, the whole of its weight resting on the lower end *k*, so that it is comparatively free to move. It is connected at *f* with the lower end of *d*, by means of a piece of caoutchouc tube covered with tape, and furnished with a screw clamp *e*. At *l* it is connected with the combustion tube *o*, by the connecting tube *l m n*, which is made of tube similar to that used for *h k*. A cork slides on *h l*, which is fitted into the lower end of a short piece of tube of a width sufficient to pass easily over the caoutchouc joint connecting the tubes at *l*. After the joint has been arranged (the ends of the tubes just touching) and bound with wire, the cork and wide tube are pushed over it and filled with glycerine. The joint at *n* is of exactly the same kind, but as it has to be frequently disconnected, water is used instead of glycerine, and the caoutchouc is not bound on to the combustion tube with wire. It will be seen that the joint at *l* is introduced chiefly to give flexibility to the apparatus. At *m* is a small bulb blown on the tube for the purpose of receiving water produced in the combustion. This is immersed in a small water trough *x*. The tube *h k* stands in a mercury trough *p*, which is shown in plan on a larger scale at B.

This trough should be cut out of a solid piece of mahogany, as it is extremely difficult to make joints to resist the pressure of such a depth of mercury. It is 200 m.m. long, 155 m.m. wide, and 100 m.m. deep, outside measurement. The edge *r r* is 13 m.m. wide, and the shelf *s* 65 m.m. wide, 174 m.m. long, and 50 m.m. deep from the top of the trough. The channel *t* is 25 m.m. wide, and 75 m.m. deep, having at one end a circular well *w*, 42 m.m. in diameter, and 90 m.m. deep. The recesses *u u* are to receive the ends of two Sprengel pumps. They are each 40 m.m. long, 25 m.m. wide, and of the same depth as the channel *t*. A short iron wire *v*, turning on a small staple, and resting at the other end against an iron pin, stretches across each of these, and serves as a kind of gate to support the test tube, in which the gas delivered by the pump is collected. The trough stands upon four legs 75 m.m. high, and is provided at the side with a tube and screw clamp *q*, by which the mercury may be drawn off to the level of the shelf *s*.

The combustion tube being placed in the furnace, protected from e direct action of the flame by a sheet-iron trough lined with bestos, and the water joint at *n* adjusted, the gas is lighted at the ont part of furnace so as to heat the whole of the metallic copper d part of the cupric oxide. A small screen of sheet iron is justed astride of the combustion tube to protect the part beyond e point up to which the gas is burning from the heat.

At the same time a stream of mercury is allowed to flow from the nnel *a*, which fills the tubes *d* and *f* until it reaches *h*, when it lls in a series of pellets down the narrow tube *h k*, each carrying fore it a quantity of air drawn from the combustion tube. The w of mercury must be controlled by means of the clamps *b* and *e*, as not to be too rapid to admit of the formation of these separate istons, and especially, care should be taken not to permit it to go fast as to mount into the connecting tube *l m n*, as it cannot be moved thence except by disconnecting the tube. During the haustion, the trough *x* is filled with hot water in order to expel om the bulb *m* any water condensed from a previous operation. about ten minutes the mercury will fall in the tube *h k* with a loud harp clicking sound, showing that the vacuum is complete. As soon s this occurs, the pump may be stopped, a test tube filled with mercury inverted over the delivery end of the tube *k*, cold water substituted for hot in the trough *x*, the iron screen removed, and the ombustion proceeded with in the usual way. This will take from fty to sixty minutes. As soon as the whole of the tube is heated o redness, the gas is turned off and the tube immediately exhausted, he gases produced being transferred to the tube placed to receive hem. When the exhaustion is complete, the test tube of gas may e removed in a small beaker, and transferred to the gas analysis pparatus.

This gas collected consists of carbonic anhydride, nitric oxide, itrogen, and (very rarely) carbonic oxide, which can readily be eparated and estimated by the ordinary methods of gas analysis. This is rapidly accomplished with the apparatus described in part 7, or the simpler form, shown in the accompanying diagram, which, whilst it does not permit of analysis by explosion, leaves nothing to be desired for this particular operation. It is essentially that described by Frankland in the Journal of the Chemical Society, ser. ii. vol. vi. p. 109 (1868), but is slightly modified in arrangement. In the diagram, *a c d* is a measuring tube, of which the cylindrical portion *a* is 370 m.m. long, and 18 m.m. in internal diameter, the part *c* 40 m.m. long, and 7 m.m. in diameter, and part *d* 175 m.m. long, and 2·5 m.m. in diameter. To the u end of *d* a tube, with a capillary bore and stopcock *f*, is attac

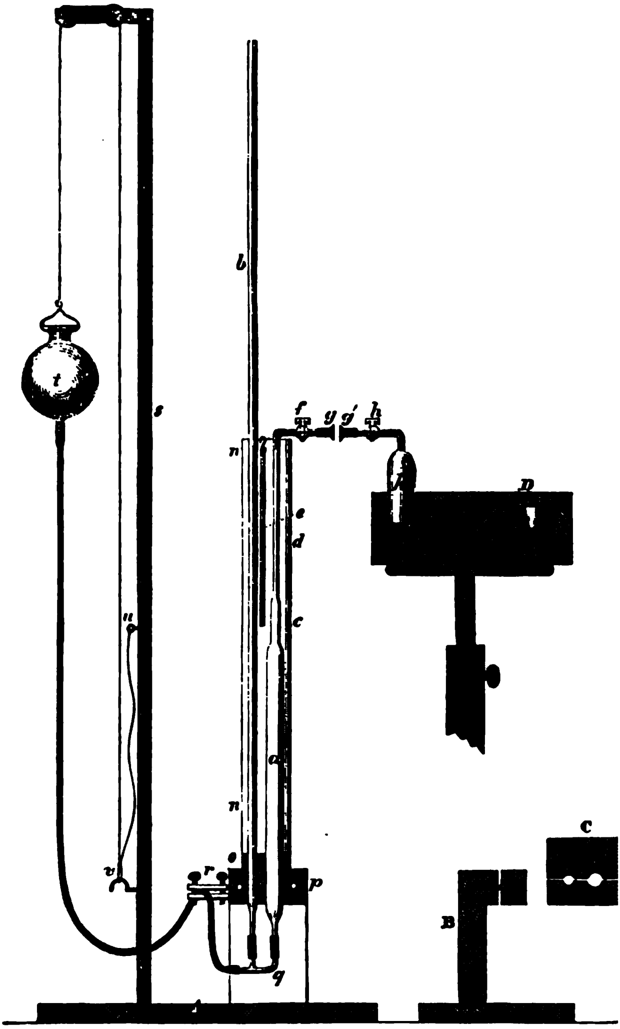

Fig. 37.

and bent at right angles. Allowing 20 m.m. for each of the co portions at the joints between *a* and *c*, and *c* and *d*, and 25 n for the vertical part of the capillary tube, the vertical measuren

the entire tube is 650 m.m. It is graduated carefully, from
ow upward, at intervals of 10 m.m., the zero being about 100
m. from the end, as about that length of it is hidden by its
pport, and therefore unavailable. The topmost 10 m.m. of *d*,
ould be divided into single millimetres. At the free end of the
pillary tube a small steel cap, shown in fig. 38, B, is cemented gas
ht. The lower end of *a* is drawn out to a diameter of 5 m.m.
e tube *b* is about 1·2 metre long, and 6 m.m. internal diameter,
drawn out like *a* at the lower end, and graduated in millimetres
m below upward, the zero being about 100 m.m. from the end.*
e tubes *a c d* and *b* pass through a caoutchouc stopper *o*, which
into the lower end of a glass cylinder *n n*, intended to contain
ter to give a definite temperature to the gas in measuring. The
os of the graduations should be about 10 m.m. above this stopper.
mediately below this the tubes are firmly clasped by the wooden
mp *p* (shown in end elevation and plan at fig. 36, B, C), the two
rts of which are drawn together by screws, the tubes being pro-
cted from injury by a piece of caoutchouc tube fitted over each.
e clamp is supported on an upright piece of wood, screwed
mly to the base A. If the stopper *o* is carefully fitted, and the
bes tightly clamped, no other support than *p* will be necessary.
e tubes below the clamp are connected by joints of caoutchouc
vered with tape and strongly bound with wire, to the vertical
s of the union piece, *q*, to the horizontal leg of which is attached
long caoutchouc tube of about 2 m.m. internal diameter, which
sses to the glass reservoir *t*. This tube must be covered with
rong tape, or (less conveniently) have a lining of canvas between
o layers of caoutchouc, as it will be exposed to considerable
essure. In its course it passes through the double screw steel
inch-cock *r*, the lower bar of which is fixed to the side of the
amp *p*. It is essential that the screws of the pinch-cock should
ave smooth collars like that shown in fig. 38, A, and that the

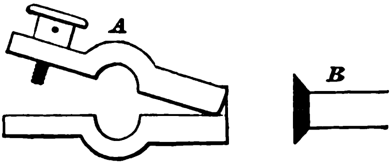

Fig. 38.

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* The graduation is not shown in the diagram.

upper surface of the upper bar of the pinch-cock should be quite flat, the surfaces between which the tube is passed being cylindrical.

In the base A is fixed a stout iron rod, 1·4 metre long, with short horizontal arm at its upper end containing two grooved pulleys. The reservoir *t* is suspended by a cord passing over these pulleys, and attached to an eye *u* in the iron rod, the length of the cord being such that, when at full stretch, the bottom of the reservoir is level with the bottom of the clamp *p*. A loop is made on the cord, which can be secured by a hook *v* on the rod, so that when thus suspended, the bottom of *t* is about 100 m.m. above the stopcock *f*. A stout elastic band fitted round *t* at its largest diameter acts usefully as a fender to protect it from an accidental blow against the iron rod. A thermometer *e*, suspended by a wire hook from the edge of the cylinder *n n*, gives the temperature of the contained water, the uniformity of which may be insured (though it is scarcely necessary) by passing a slow succession of bubbles of air through it, or by moving up and down in it a wire with its end bent into the form of a ring. The jar *k* is called the laboratory vessel, and is 100 m.m. high, and 38 m.m. in internal diameter, having a capillary tube, glass stopcock, and steel cap *g′* exactly like *f g*. The mercury trough *l* is shown in figs. 39 and 40. It is of solid mahogany, 265 m.m. long, 80 m.m. broad, and 90 m.m. deep, outside measurement. The rim *a a a a* is 8 m.m. broad, and 15 m.m. deep. The excavation *b* is 230 m.m. long, 26 m.m. broad, and 65 m.m. deep, with a circular cavity to receive the laboratory vessel sunk at one end, 45 m.m. in diameter, and 20 m.m. in depth below the top of the excavation. Two small lateral indentations *c c*, fig. 40, near the other end accommodate a capsule for transferring to the trough, tubes containing gas. This trough rests upon a telescope table, which can be fixed at any height by means of a screw, and is supported on three feet. It must be arranged, so that when the laboratory vessel is in its place in the trough, the two steel caps exactly correspond face to face.

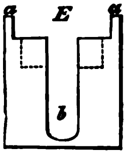


Fig. 39.

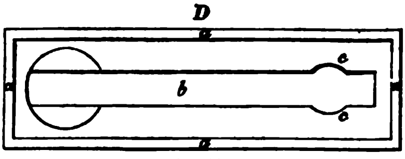


Fig. 40.

The difference of level of the mercury in the tubes *b* and *a c d*, caused by capillary action, when both are freely open to the air must be ascertained by taking several careful observations. This will be different for each of the portions *a c* and *d*, and must be added to or deducted from the observed pressure, as the mercury when thus freely exposed in both tubes to the atmospheric pressure stands in *a c* or *d* above or below that in *b*. This correction will include also any that may be necessary for difference of level of the zeros of the graduations of the two tubes, and, if the relative positions of these be altered, it must be redetermined. A small telescope, sliding on a vertical rod, should be used in these and all other readings of the level of mercury.

The capacity of the measuring tube *a c d* at each graduation must now be determined. This is readily done by first filling the whole apparatus with mercury, so that it drips from the cap *g*. The stopcock *f* is then closed, a piece of caoutchouc tube slipped over the cap, and attached to a funnel supplied with distilled water. The reservoir *t* being lowered, the clamp *r* and the stopcock *f* are opened, so that the mercury returns to the reservoir, water entering through the capillary tube. As soon as it is below the zero of the graduation, the stopcock *f* is closed, the funnel and caoutchouc tube removed from the cap, and the face of the last slightly greased in order that water may pass over it without adhering. Now raise the reservoir, open the stopcock *f*, and allow the water to flow gently out until the top of the convex surface of the mercury in *a* just coincides with the zero of the graduation. The mercury should be controlled by the clamp *r*, so that the water issues under very slight pressure. Note the temperature of the water in the water jacket, and proceed with the expulsion of the water, collecting it as it drops from the steel cap in a small carefully weighed glass flask. When the mercury has risen through 100 m.m. stop the flow of water, and weigh the flask. The weight of water which was contained between the graduations 0 and 100 on the tube is then known, and if the temperature be 4° C., the weight in grammes will express the capacity of that part of the tube in cubic centimetres. If the temperature be other than 4° C., the volume must be calculated by the aid of the co-efficient of expansion of water by heat. In a similar way the capacity of the tube at successive graduations about 100 m.m. apart is ascertained, the last determination in *a* being at the highest, and the first in *c* at the lowest graduation on the cylindrical part of each tube; the tube between these points and similar points on *c* and *d* being so distorted by the glass blower that observations could not well be made. The capacity at a sufficient number of points being ascertained, that at each of the intermediate graduations may be calculated, and a table arranged with the capacity marked against each graduation. As the calculations in the analysis are made by the aid of logarithms, it is convenient to enter on this table the logarithms of the capacities instead of the natural numbers.

In using the apparatus, the stopcocks on the measuring tube and laboratory vessel should be slightly greased with a mixture of resin cerate and oil, the whole apparatus carefully filled with mercury, and the stopcock *f* closed; next place the laboratory vessel in position in the mercury trough, and suck out the air. This is readily and rapidly done by the aid of a short piece of caoutchouc tube, placed in the vessel just before it is put into the mercury trough, and drawn away as soon as the air is removed. Suck out any small bubbles of air still left through the capillary tube, and as soon as the vessel is entirely free from air close the stopcock. Slightly grease the faces of both caps with resin cerate (to which a little oil should be added if very stiff), and clamp them tightly together. On opening both stopcocks mercury should flow freely through the capillary communication thus formed, and the whole should be quite free from air. To ascertain if the joints are all in good order, close the stopcock *h*, and lower the reservoir *t* to its lowest position; the joints and stopcocks will thus be subjected to a pressure of nearly half an atmosphere, and any leakage would speedily be detected. If all be right, restore the reservoir to its upper position.

Transfer the tube containing the gas to be analysed to an ordinary porcelain mercury trough, exchange the beaker in which it has been standing for a small porcelain capsule, and transfer it to the mercury trough *l*, the capsule finding ample room where the trough is widened by the recess D.

Carefully decant the gas to the laboratory vessel, and add a drop or two of potassic bichromate solution (B. η.) from a small pipette with a bent capillary delivery tube, to ascertain if the gas contains any sulphurous anhydride. If so, the yellow solution will immediately become green from the formation of a chromic salt, and the gas must be allowed to stand over the chromate for four or five minutes, a little more of the solution being added if necessary. The absorption may be greatly accelerated by gently shaking from time to time the stand on which the mercury trough rests, so as to cause the solution to wet the sides of the vessel. With care this may be done without danger to the apparatus. Mercury should be allowed to pass slowly into the laboratory vessel during the whole time, as the drops falling tend to maintain a circulation both in the gas and in the absorbing liquid. The absence of sulphurous anhydride being ascertained, both stopcocks are set fully open, the reservoir *t* lowered, and the gas transferred to the measuring tube. The stopcock *h* should be closed as soon as the liquid from the laboratory vessel is within about 10 m.m. of it. The bore of the capillary tube is so fine that the quantity of gas contained in it is too small to affect the result. Next bring the top of the meniscus of mercury seen through the telescope exactly to coincide with one of the graduations on the measuring tube, the passage of mercury to or from the reservoir being readily controlled by the pinchcock *r*. Note the position of the mercury in the measuring tube and in the pressure tube *b*, the temperature of the water-jacket, and the height of the barometer, the level of the mercury in the pressure tube and barometer being read to a tenth of a m.m. and the thermometer to 0·1° C. This done, introduce into the laboratory vessel from a pipette with a bent point, a few drops of potassic hydrate solution (B. *θ*.), and return the gas to the laboratory vessel. The absorption of carbonic anhydride will be complete in about three to five minutes, and if the volume of the gas is large, may be much accelerated by gently shaking the stand from time to time, so as to throw up the liquid on the sides of the vessel. If the small pipettes used to introduce the various solutions are removed from the mercury trough gently, they will always contain a little mercury in the bend, which will suffice to keep the solution from flowing out, and they may be kept in readiness for use standing upright in glass cylinders or other convenient supports. At the end of five minutes the gas, which now consists of nitrogen and nitric oxide, is again transferred to the measuring tube, and the operation of measuring repeated; the barometer, however, need not be observed, under ordinary circumstances, more than once for each analysis, as the atmospheric pressure will not materially vary during the twenty-five to thirty minutes required. Next pass into the laboratory vessel a few drops of saturated solution of pyrogallic acid (B. *ι*.), and return the gas upon it. The object of adding the pyrogallic acid at this stage is to ascertain if oxygen is present, as sometimes happens when the total quantity of gas is very small, and the vacuum during the combustion but slightly impaired. Under such circumstances, traces of oxygen are given off by the cupric oxide, and pass so rapidly over the metallic copper as to escape absorption. This necessarily involves the loss of any nitric oxide which also escapes the copper, but this is such a very small proportion of an already small quantity that its loss will not appreciably affect the result. If oxygen be present, allow the gas to remain exposed to the action of the pyrogallate until the liquid when thrown up the sides of the laboratory vessel runs off without leaving a dark red stain. If oxygen be not present, a few bubbles of that gas (B. λ.) are introduced to oxidize the nitric oxide to pernitric oxide, which is absorbed by the potassic hydrate. The oxygen may be very conveniently added from the gas pipette shown in fig. 41, where *a b* are glass bulbs of about 50 m.m. diameter, connected by a glass tube, the bore of which is constricted at *c*, so as to allow mercury to pass but slowly from one bulb to the other, and thus control the passage of gas through the narrow delivery tube *d*. The other end *e* is provided with a short piece of caoutchouc tube, by blowing through which any desired quantity of gas may be readily delivered. Care must be taken after use that the delivery tube is not removed from the trough until the angle *d* is filled with mercury.

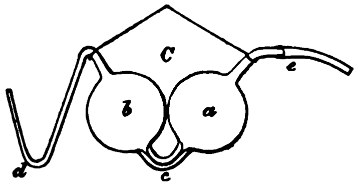


Fig. 41.

To replenish the pipette with oxygen, fill the bulb *b* and the tubes *c* and *d* with mercury, introduce the point of *d* into a tube of oxygen standing in the mercury trough, and draw air from the tube *e*. The gas in *b* is confined between the mercury in *c* and that in *d*.

When the excess of oxygen has been absorbed as above described, the residual gas, which consists of nitrogen, is measured, and the analysis is complete.*

There are thus obtained three sets of observations, from which by usual methods we may calculate A the total volume, B the ne of nitric oxide and nitrogen, and C the volume of nitrogen, all ed to 0° C. and 760 m.m. pressure; from these may be obtained

---

* When the quantity of carbon is very large indeed, traces of carbonic oxide are occasionally present in the gas, and will remain with the nitrogen after treatment with alkaline pyrogallate. When such excessive quantities of carbon are found, the stopcock *f* should be closed when the last measurement is made, the laboratory vessel detached, washed, and replaced filled with mercury. Introduce then a little solution of cuprous chloride (B. κ.), and return the gas upon it. Any carbonic oxide will be absorbed, and after about five minutes the remaining nitrogen may be measured. In more than twenty consecutive analyses of waters of very varying kinds, not a trace of carbonic oxide was found in any of the gases obtained on combustion.

$$A - B = \text{vol. of } CO^2,$$

$$\frac{B - C}{2} + C = \frac{B + C}{2} = \text{vol. of N},$$

ence the weight of carbon and nitrogen can be readily found. is much less trouble, however, to assume that the gas in all stages consists wholly of nitrogen; then, if A be the weight e total gas, B its weight after treatment with potassic hydrate, after treatment with pyrogallate, the weight of carbon will $- B)\frac{3}{7}$ and the weight of nitrogen $\frac{B + C}{2}$, for the weights of n and nitrogen in equal volumes of carbonic anhydride and gen, at the same temperature and pressure, are as 6 : 14; and eights of nitrogen in equal volumes of nitrogen and nitric are as 2 : 1.

e weight of 1 c.c. of nitrogen at 0° C. and 760 m.m. is 0·0012562 nd the formula for the calculation is $w = \frac{0{\cdot}0012562 \times v \times p}{(1 + 0{\cdot}00367t)\,760}$, ich w = the weight of nitrogen, v the volume, p the pressure ted for tension of aqueous vapour, and t the temperature in es centigrade. To facilitate this calculation, there is given in 2 the logarithmic value of the expression $\frac{0{\cdot}0012562}{(1 + 0{\cdot}00367\,t)\,760}$ ch tenth of a degree from 0° to 29·9° C, and in Table 1 the n of aqueous vapour in millimetres of mercury. As the uring tube is always kept moist with water, the gas when ured is always saturated with aqueous vapour.

e following example will show the precise mode of calculation:—

	A Total.	B After absorption of CO^2.	C Nitrogen.
e of gas, ...	4·4888 c.c.	0·26227 c.c.	0·26227 c.c.
erature, ...	13·5°	13·6°	13·7°
	m.m.		
t of mercury in *a*,*c*,*d*,	310·0	480·0	480·0
,, ,, *b*,	193·5	343·5	328·2
Difference, . . .	116·5	136·5	151·8
tension of aqueous our	11·5	11·6	11·7
	128·0		
t correction for capil- ty, ...	0·9	Add for capillarity } 2·2	2·2
	127·1	150·3	165·7

	A	B	C
	Total.	After absorption of CO².	Nitrogen.
Deduct this from height of barometer, ...	769·8 127·1	769·8 150·3	769·8 165·7
Tension of dry gas, . . .	642·7	619·5	604·1
Log. of volume of gas, . .	$\bar{0}$·65213	$\bar{1}$·41875	$\bar{1}$·41875
" $\frac{0·0012562}{(1 + 0·00367\,t)\ 760}$	$\bar{6}$·19724	$\bar{6}$·19709	$\bar{6}$·19694
,, tension of dry gas,	2·80801	2·79204	2·78111
Log. of weight of gas calculated as N, ...	$\bar{3}$·65738 =0·0045434	$\bar{4}$·40788 0·0002558	$\bar{4}$·39680 0·0002494 gm.

From these weights, those of carbon and of nitrogen are obtained by the use of the formulæ above mentioned. Thus—

A − B = 0·0042876
× 3
÷ 7)0·0128628
Weight of carbon, 0·001837

B + C = 0·0005052
÷ 2
Weight of nitrogen, 0·0002526

When carbonic oxide is found, the corresponding weight of nitrogen may be found in a similar manner, and should be added to that corresponding to the carbonic anhydride before multiplying by $\frac{3}{7}$, and must be deducted from the weight corresponding to the volume after absorption of carbonic anhydride.

As it is impossible to attain to absolute perfection of manipulation and materials, each analyst should make several blank experiments by evaporating a litre of pure distilled water (B. *a.*) with the usual quantities of sulphurous acid and chloride of iron, and, in addition, 0·1 gm. of freshly ignited sodic chloride (in order to furnish a tangible residue). The residue should be burnt and analysed in the usual way, and the average amounts of carbon and nitrogen thus obtained deducted from the results of all analyses. This correction, which may be about 0·0001 gm. of C., and 0·00005 gm. of N, includes the errors due to imperfection of the vacuum produced by the Sprengel pump, nitrogen retained in the cupric oxide, ammonia absorbed from the atmosphere during evaporation, &c.

When the quantity of nitrogen as ammonia exceeds 0·007 pt. per 100,000, there is a certain amount of loss of nitrogen during the evaporation by dissipation of ammonia. This appears to be very constant, and is given in Table 3, which is calculated from Table 5, which has been kindly furnished by Dr. Frankland.

The number in this table corresponding to the quantity of nitrogen as ammonia present in the water analysed should be added to the amount of nitrogen found by combustion. The number thus obtained includes the nitrogen as ammonia, and this must be deducted to ascertain the *organic* nitrogen. If "ammonia" is determined instead of "nitrogen as ammonia" Table 5 may be used.

When, in operating upon sewage, hydric metaphosphate has been employed, Tables 4 or 6 should be used.

Rules for Converting Parts per 100,000 into Grains per Gallon, or the reverse.

To convert parts per 100,000 into grains per gallon, multiply by 0·7.

To convert grains per gallon into parts per 100,000, divide by 0·7.

To convert grammes per litre into grains per gallon, multiply by 70.

TABLE 1.

Elasticity of Aqueous Vapour for each $\frac{1}{10}$th degree centigr from 0° to 30° C. (Regnault).

Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.	Temp. C.	Tension in Millimetres of Mercury.
0°	4·6	6·0°	7·0	12·0°	10·5	18·0°	15·4	24·0°	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·8	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4·9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	·5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8·5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8·5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	·7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

TABLE 2.

ction of Cubic Centimetres of Nitrogen to Grammes.

$\frac{0{\cdot}0012562}{(1+0{\cdot}00367t)760}$ for each tenth of a degree from 0° to 30°. C.

0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
·21824	808	793	777	761	745	729	713	697	681
665	649	633	617	601	586	570	554	538	522
507	491	475	459	443	427	412	396	380	364
349	333	318	302	286	270	255	239	223	208
192	177	161	145	130	114	098	083	067	051
035	020	004	*989	*973	*957	*942	*926	*911	*895
·20879	864	848	833	817	801	786	770	755	739
723	708	692	676	661	645	629	614	598	583
567	552	536	521	505	490	474	459	443	428
413	397	382	366	351	335	320	304	289	274
259	244	228	213	198	182	167	151	136	121
106	090	075	060	045	029	014	*999	*984	*969
·19953	938	923	907	892	877	862	846	831	816
800	785	770	755	740	724	709	694	679	664
648	633	618	603	588	573	558	543	528	513
497	482	467	452	437	422	407	392	377	362
346	331	316	301	286	271	256	241	226	211
196	181	166	151	136	121	106	091	076	061
046	031	016	001	*986	*971	*956	*941	*926	*911
·18897	882	867	852	837	822	807	792	777	762
748	733	718	703	688	673	659	644	629	614
600	585	570	555	540	526	511	496	481	466
452	437	422	408	393	378	363	349	334	319
305	290	275	261	246	231	216	202	187	172
158	143	128	114	099	084	070	055	041	026
012	*997	*982	*968	*953	*938	*924	*909	*895	*880
·17866	851	837	822	808	793	779	764	750	735
721	706	692	677	663	648	634	619	605	590
576	561	547	532	518	503	489	475	460	446
432	417	403	388	374	360	345	331	316	302

TABLE 3.

Loss of Nitrogen by Evaporation of NH^3.
With Sulphurous Acid.

Parts per 100,000.

N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3.	Loss of N.
5·0	1·741	3·9	1·425	2·8	·898	1·7	·370	·6	·145	·04	·009
4·9	1·717	3·8	1·378	2·7	·850	1·6	·338	·5	·109	·03	·007
4·8	1·693	3·7	1·330	2·6	·802	1·5	·324	·4	·075	·02	·005
4·7	1·669	3·6	1·282	2·5	·754	1·4	·309	·3	·057	·01	·003
4·6	1·645	3·5	1·234	2·4	·706	1·3	·295	·2	·038	·008	·002
4·5	1·621	3·4	1·186	2·3	·658	1·2	·280	·1	·020	·007	·001
4·4	1·598	3·3	1·138	2·2	·610	1·1	·266	·09	·018		
4·3	1·574	3·2	1·090	2·1	·562	1·0	·252	·08	·017		
4·2	1·550	3·1	1·042	2·0	·514	·9	·237	·07	·015		
4·1	1·521	3·0	·994	1·9	·466	·8	·217	·06	·013		
4·0	1·473	2·9	·946	1·8	·418	·7	·181	·05	·011		

TABLE 4.

Loss of Nitrogen by Evaporation of NH^3.
With Hydric Metaphosphate.

Parts per 100,000.

Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.	Volume evaporated.	N as NH^3.	Loss of N.
100 c.c.	8·2	·482	100 c.c.	5·9	·385	100 c.c.	3·6	·281	100 c.c.	1·3	·142
...	8·1	·477	...	5·8	·381	...	3·5	·277	...	1·2	·136
...	8·0	·473	...	5·7	·377	...	3·4	·272	...	1·1	·129
...	7·9	·469	...	5·6	·373	...	3·3	·267	...	1·0	·123
...	7·8	·465	...	5·5	·368	...	3·2	·261	...	·9	·117
...	7·7	·461	...	5·4	·364	...	3·1	·255	...	·8	·111
...	7·6	·456	...	5·3	·360	...	3·0	·249	250 c.c.	·7	·088
...	7·5	·452	...	5·2	·356	...	2·9	·242	...	·6	·073
...	7·4	·448	...	5·1	·352	...	2·8	·236	...	·5	·061
...	7·3	·444	...	5·0	·347	...	2·7	·230	500 c.c.	·4	·049
...	7·2	·440	...	4·9	·343	...	2·6	·223	...	·3	·036
...	7·1	·435	...	4·8	·338	...	2·5	·217	1000 c.c.	·2	·024
...	7·0	·431	...	4·7	·334	...	2·4	·211	...	·1	·012
...	6·9	·427	...	4·6	·329	...	2·3	·205	...	·09	·011
...	6·8	·423	...	4·5	·324	...	2·2	·198	...	·08	·010
...	6·7	·419	...	4·4	·319	...	2·1	·192	...	·07	·008
...	6·6	·414	...	4·3	·315	...	2·0	·186	...	·06	·007
...	6·5	·410	...	4·2	·310	...	1·9	·180	...	·05	·006
...	6·4	·406	...	4·1	·305	...	1·8	·173	...	·04	·005
...	6·3	·402	...	4·0	·301	...	1·7	·167	...	·03	·004
...	6·2	·398	...	3·9	·296	...	1·6	·161	...	·02	·002
...	6·1	·394	...	3·8	·291	...	1·5	·154	...	·81	·001
...	6·0	·389	...	3·7	·286	...	1·4	·148			

TABLE 5.

Loss of Nitrogen by Evaporation of NH^3.
With Sulphurous Acid.
Parts per 100,000.

NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3.	Loss of N.
6·0	1·727	4·8	1·451	3·6	·977	2·4	·503	1·2	·250	·09	·014
5·9	1·707	4·7	1·411	3·5	·937	2·3	·463	1·1	·238	·08	·013
5·8	1·688	4·6	1·372	3·4	·898	2·2	·424	1·0	·226	·07	·012
5·7	1·668	4·5	1·332	3·3	·858	2·1	·384	·9	·196	·06	·010
5·6	1·648	4·4	1·293	3·2	·819	2·0	·345	·8	·166	·05	·009
5·5	1·628	4·3	1·253	3·1	·779	1·9	·333	·7	·136	·04	·007
5·4	1·609	4·2	1·214	3·0	·740	1·8	·321	·6	·106	·03	·006
5·3	1·589	4·1	1·174	2·9	·700	1·7	·309	·5	·077	·02	·004
5·2	1·569	4·0	1·135	2·8	·661	1·6	·297	·4	·062	·01	·003
5·1	1·549	3·9	1·095	2·7	·621	1·5	·285	·3	·047	·009	·001
5·0	1·530	3·8	1·056	2·6	·582	1·4	·274	·2	·032		
4·9	1·490	3·7	1·016	2·5	·542	1·3	·262	·1	·017		

TABLE 6.

Loss of Nitrogen by Evaporation of NH^3.
With Hydric Metaphosphate.
Parts per 100,000.

Volume evaporated.	NH_3.	Loss of N.	Volume evaporated.	NH_3.	Loss of N.	Volume evaporated.	NH_3.	Loss of N.	Volume evaporated.	NH_3.	Loss of N.
100 c.c.	10·0	·483	100 c.c.	7·2	·386	100 c.c.	4·4	0·283	100 c.c.	1·6	·143
...	9·9	·480	...	7·1	·382	...	4·3	0·279	...	1·5	·137
...	9·8	·476	...	7·0	·379	...	4·2	0·275	...	1·4	·132
...	9·7	·473	...	6·9	·375	...	4·1	0·271	...	1·3	·127
...	9·6	·469	...	6·8	·372	...	4·0	0·267	...	1·2	·122
...	9·5	·466	...	6·7	·368	...	3·9	0·262	...	1·1	·117
...	9·4	·462	...	6·6	·365	...	3·8	0·257	...	1·0	·112
...	9·3	·459	...	6·5	·361	...	3·7	0·252	250 c.c.	0·9	·096
...	9·2	·455	...	6·4	·358	...	3·6	0·247	...	0·8	·080
...	9·1	·452	...	6·3	·354	...	3·5	0·242	...	0·7	070
...	9·0	·448	...	6·2	·351	...	3·4	0·236	...	0·6	·060
...	8·9	·445	...	6·1	·348	...	3·3	0·231	500 c.c.	0·5	·050
...	8·8	·441	...	6·0	·345	...	3·2	0·226	...	0·4	·040
...	8·7	·438	...	5·9	·341	...	3·1	0·221	...	0·3	·030
...	8·6	·434	...	5·8	·337	...	3·0	0·216	1000 c.c.	0·2	·020
...	8·5	·431	...	5·7	·333	...	2·9	0·211	...	0·1	·010
...	8·4	·428	...	5·6	·330	...	2·8	0·205	...	0·09	·009
...	8·3	·424	...	5·5	·326	...	2·7	0·200	...	0·08	·008
...	8·2	·421	...	5·4	·322	...	2·6	0·195	...	0·07	·007
...	8·1	·417	...	5·3	·318	...	2·5	0·190	...	0·06	·006
...	8·0	·414	...	5·2	·314	...	2·4	0·184	...	0·05	·005
...	7·9	·410	...	5·1	·310	...	2·3	0·179	...	0·04	·004
...	7·8	·407	...	5·0	·306	...	2·2	0·174	...	0·03	·003
...	7·7	·403	...	4·9	·302	...	2·1	0·169	...	0·02	·002
...	7·6	·400	...	4·8	·298	...	2·0	0·164	...	0·01	·001
...	7·5	·396	...	4·7	·294	...	1·9	0·158			
...	7·4	·393	...	4·6	·291	...	1·8	0·153			
...	7·3	·389	...	4·5	·287	...	1·7	0·148			

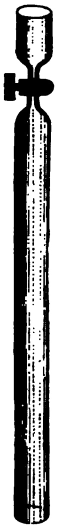
5. Estimation of Total Solid Matter.

Evaporate over a steam or water bath half a litre or a less quantity of the water in a platinum dish which has been heated to redness and carefully weighed. The water should be filtered or unfiltered, according to the decision made in that respect at the commencement of the analysis. The quantity to be taken is regulated chiefly by the amount of nitrate present, as the residue from this operation is, with certain exceptions, employed for the determination of the nitrogen as nitrates and nitrites. As a general rule, for water supplies and river water half a litre should be used; for shallow well waters, a quarter of a litre. Of sewages, 100 c.c., and of waters containing more than 0·08 pt. of nitrogen as ammonia per 100,000, a quarter of a litre will generally be convenient, as in these cases the residue will not be used for the estimation of nitrogen as nitrates and nitrites; and the only point to be considered is to have a quantity of residue suitable to weigh. It is desirable to support the platinum dish during evaporation in a glass ring with a flange, shaped like the top of a beaker, the cylindrical part being about 20 m.m. deep. This is dropped into the metal ring on the water bath, and thus lines the metal with glass and keeps the dish clean. A glass disc with a hole in it to receive the dish is not satisfactory, as drops of water conveying solid matter find their way across the under surface from the metal vessel to the dish, and thus soil it. As soon as the evaporation is complete, the dish with the residue is removed, its outer side wiped dry with a cloth, and it is dried in a water or steam oven for about three hours. It is then removed to a desiccator, allowed to cool, weighed as rapidly as possible, returned to the oven and weighed at intervals of an hour, until between two successive weighings it has lost less than 0·001 gm.

6. Estimation of Nitrogen as Nitrates and Nitrites.

The residue obtained in the preceding operation may be used for this estimation. Treat it with about 30 c.c. of hot distilled water, taking care to submit the whole of the residue to its action. Add solution of argentic sulphate (C. *a.*) until the chlorine is entirely precipitated, and heat on the steam bath for a few minutes. Then filter through a very small filter of Swedish paper, washing the dish several times with small quantities of hot distilled water.

It is advisable to rub the dish gently with the finger, so as to tach the solid matter as far as possible, and thus expose it oroughly to the action of the water. The finger should be protected by a caoutchouc finger stall, or it will be stained by the silver. Test the filtrate with a drop of argentic sulphate to ascertain if the whole of the chlorine has been precipitated. This may be known before filtration, as a rule, by the residue becoming dark brown whilst on the steam bath. The platinum dish is readily cleaned after use by immersing it in dilute sulphuric acid, and placing in contact with it a piece of zinc. In a few minutes the argentic chloride present is reduced to the metallic state, and may be entirely dissolved by warm nitric acid. This acid should be kept for this purpose until highly charged with argentic nitrate, and the silver then recovered from it.


ig. 42.

The filtrate must be evaporated in a very small beaker, over a steam bath, until reduced to about 1 c.c., or even to dryness. This concentrated solution is introduced into the glass tube shown in fig. 42, standing in the porcelain mercury trough, filled up to the stopcock with mercury. The tube is 210 m.m. in total length, and 15 m.m. in ternal diameter. By pouring the liquid into the cup at the top, d then cautiously opening the stopcock, it may be run into the be without admitting any air. The beaker is rinsed once with a ry little hot distilled water, and then two or three times with ong sulphuric acid (C. β.), the volume of acid being to that of e aqueous solution about as 3 : 2. The total volume of acid and ter should be about 6 c.c. Should any air by chance be admit- l at this stage, it may readily be removed by suction, the lips ing applied to the cup. With care there is but little danger of tting acid into the mouth.

In a few cases carbonic anhydride is given off on addition of lphuric acid, and must be sucked out before proceeding.

Now grasp the tube firmly in the hand, closing the open end by e thumb, which should be first moistened; withdraw it from the ugh, incline it at an angle of about 45°, the cup pointing from u, and shake it briskly with a rapid motion in the direction of length, so as to throw the mercury up towards the stopcock. fter a very little practice there is no danger of the acid finding way down to the thumb, the mixture of acid and mercury being confined to a comparatively small portion of the tube. In a few seconds some of the mercury becomes very finely divided; and if nitrates be present, in about a minute or less, nitric oxide is evolved, exerting a strong pressure on the thumb. Mercury is allowed to escape as the reaction proceeds, by partially, but not wholly, relaxing the pressure of the thumb. A slight excess of pressure should be maintained within the tube to prevent entrance of air during the agitation, which must be continued until no more gas is evolved.

When the quantity of nitrate is very large, the mercury, on shaking, breaks up into irregular masses, which adhere to one another as if alloyed with lead or tin, and the whole forms a stiff dark-coloured paste, which it is sometimes very difficult to shake, but nitric oxide is not evolved for a considerable time, then comes off slowly, and afterwards with very great rapidity. To have room for the gas evolved, the operator should endeavour to shake the tube so as to employ as little as possible of the contained mercury in the reaction. At the close of the operation the finely-divided mercury will consist for the most part of minute spheres, the alloyed appearance being entirely gone. An experiment with a large quantity of nitrate may often be saved from loss by firmly resisting the escape of mercury, shaking until it is judged by the appearance of the contents of the tube that the reaction is complete, and then on restoring the tube to the mercury trough, allowing the finely-divided mercury also to escape in part. If the gas evolved be not more than the tube will hold, and there be no odour of pernitric oxide from the escaped finely-divided mercury, the operation may be considered successful. If the amount of nitrate be too large, a smaller quantity of the water must be evaporated and the operation repeated. When no nitrate is present, the mercury usually manifests very little tendency to become divided, that which does so remains bright, and the acid liquid does not become so turbid as it does in other cases.

The reaction completed, the tube is taken up covered by the thumb, and the gas is decanted into the laboratory vessel, and measured in the usual way in the gas apparatus. The nitric acid tube is of such a length, that when the cup is in contact with the end of the mercury trough, the open end is just under the centre of the laboratory vessel. If any acid has been expelled from the tube at the close of the shaking operation, the end of the tube and the thumb should be washed with water before introducing into he mercury trough of the gas apparatus, so as to remove any acid which may be adhering, which would destroy the wood of the rough. Before passing the gas into the measuring tube of the gas pparatus, a little mercury should be allowed to run over into the aboratory vessel to remove the acid from the entrance to the apillary tube.

As nitric oxide contains half its volume of nitrogen, if half a itre of water has been employed, the volume of nitric oxide obained will be equal to the volume of *nitrogen* present as nitrates nd nitrites in one litre of the water, and the weight of the nitrogen may be calculated as directed in the paragraph on the stimation of organic carbon and nitrogen.

When more than 0·08 part of nitrogen as ammonia is present in 00,000 parts of liquid, there is danger of loss of nitrogen by lecomposition of ammonic nitrite on evaporation; and therefore he residue from the estimation of total solid matter cannot be used. In such cases acidify a fresh quantity of the liquid with lilute hydric sulphate, add solution of potassic permanganate, a ittle at a time, until the pink colour remains for about a minute, nd render the liquid just alkaline to litmus paper with sodic arbonate. The nitrites present will then be converted into nitrates, and may be evaporated without fear of loss. Use as little f each re-agent as possible. Sewage may be examined in this way; but it is hardly necessary to attempt the determination, as ewage is almost invariably free from nitrates and nitrites. Out of everal hundred specimens, the writer only found two or three which contained any, and even then only in very small quantity.

. Estimation of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, with but little Ammonia or Organic Nitrogen.

When the quantity of soluble matter is excessive, as, for example, n sea-water, the preceding method is inapplicable, as the solution o be employed cannot be reduced to a sufficiently small bulk to go nto the shaking tube. If the quantity of organic nitrogen be less han 0·1 part in 100,000, the nitrogen as nitrates and nitrites may enerally be determined by the following modification of Schulze's method, devised by E. T. Chapman. To 200 c.c. of the water add 10 c.c. of sodic hydrate solution (C. ζ.), and boil briskly in an open porcelain dish until it is reduced to about 70 c.c. When cold pour the residue into a tall glass cylinder of about 120 c.c. capacity, and rinse the dish with water free from ammonia. Add a piece of aluminium foil of about 15 sq. centim. area, loading it with a piece of clean glass rod to keep it from floating. Close the mouth of the cylinder with a cork, bearing a small tube filled with pumice (C. η.) moistened with hydric chloride free from ammonia (C. θ.).

Hydrogen will speedily be given off from the surface of the aluminium, and in five or six hours the whole of the nitrogen as nitrates and nitrites, will be converted into ammonia. Transfer to a small retort the contents of the cylinder, together with the pumice, washing the whole apparatus with a little water free from ammonia. Distil, and estimate ammonia in the usual way with Nessler solution. It appears impossible wholly to exclude ammonia from the re-agents and apparatus, and therefore some blank experiments should be made to ascertain the correction to be applied for this. This correction is very small, and appears to be nearly constant.

8. Estimation of Nitrogen as Nitrates and Nitrites by the Indigo Process.

Although this method cannot compete with the mercury process as regards accuracy, yet it promises to be very useful in cases where extreme accuracy is not required, and its simplicity and rapidity are greatly in its favour. Moreover, the costly gas analysis apparatus used in the former process is not required.

The operation is conducted as described at pp. 112, 113, but it is convenient to use the weaker solutions described at p. 288, (C. ι, κ.). The water is taken without any preparation, about 10 or 20 c.c. being used for each experiment. If 10 c.c. require more than about 15 or 20 c.c. of indigo (C. κ.), it is better to repeat the experiment with a smaller volume of the water, as it is inconvenient to use a large quantity of indigo. In order to test the process as applied to water analysis, the nitrogen as nitrates and nitrites was determined both by the mercury and indigo methods in ten samples of water selected to represent as far as possible very

liffering kinds of water. The following are the results
:—

	With Mercury.	With Indigo.
	Parts per 100,000.	
1	·973	·912
2	4·335	4·530
3	1·825	1·706
4	·729	·676
5	2·749	2·912
6	1·696	1·294
7	2·114	2·265
8	·354	·338
9	2·860	2·824
10	·222	·221

9. Estimation of Suspended Matter.

: of Swedish paper, about 110 m.m. in diameter, are ıne inside another, about 15 or 20 together, so that water ; through the whole group, moistened with dilute hydrocid, washed with hot distilled water until the washings ɔontain chlorine, and dried. The ash of the paper is thus by about 60 per cent., and must be determined for each filter paper by incinerating 10 filters, and weighing the r use in estimating suspended matter, these washed filters dried for several hours at 120–130° C., and each one then at intervals of an hour until the weight ceases to diminish, t until the loss of weight between two consecutive weighnot exceed 0·0003 gm. It is most convenient to enclose ' during weighing in two short tubes fitting closely one ɔther. The closed ends of test tubes, 50 m.m. long, cut ading a crack round with the aid of a pastille or very ; jet, the sharp edges being afterwards fused at the blowwer perfectly. Each pair of tubes should have a distincber, which is marked with a diamond on both tubes. In ıth they should rest in grooves formed by a folded sheet the tubes being drawn apart, and the filter almost, but ;, out of the smaller tube. They can then be shut up ıt by gently pushing the tubes together, being guided by 'ed paper. They require to remain about twenty minutes ɔcator to cool before weighing. Filtration will be much ɔd if the filters be ribbed before drying. As a general vill be sufficient to filter a quarter of a litre of a sewage, re of a highly polluted river, and a litre of a less polluted water; but this must be frequently varied to suit individual cases. Filtration is hastened, and trouble diminished, by putting the liquid to be filtered into a narrow-necked flask, which is inverted into the filter, being supported by a funnel-stand, the ring of which has a slot cut through it to allow the neck of the flask to pass. With a little practice the inversion may be accomplished without loss, and without previously closing the mouth of the flask. When all has passed through, the flask should be rinsed out with distilled water, and the rinsings added to the filter. Thus any particles of solid matter left in the flask are secured, and the liquid adhering to the suspended matter and filter is displaced. The filtrate from the washings should not be added to the previous filtrate, which may be employed for determination of total solid matter, chlorine, hardness, &c.

Thus washed, the filter with the matter upon it is dried at 100° C., then transferred from the funnel to the same pair of tubes in which it was previously weighed, and the operation of drying at 120°-130° C. and weighing until constant repeated. The weight thus obtained, minus the weight of the empty filter and tubes, gives the weight of the total suspended matter dried at 120°-130° C.

To ascertain the quantity of mineral matter in this, the filter with its contents is incinerated in a platinum crucible, and the total ash thus determined, minus the ash of the filter alone, gives the weight of the mineral suspended matter.

10. Estimation of Chlorine present as Chloride.

To 50 c.c. of the water add two or three drops of solution of potassic chromate (D. β.), so as to give it a faint tinge of yellow, and add gradually from a burette standard solution of argentic nitrate (D. α.) until the red argentic chromate which forms after each addition of the nitrate ceases to disappear on shaking. The number of c.c. of silver solution employed will express the chlorine present as chloride in parts in 100,000. If this amount be much more than 10, it is advisable to take a smaller quantity of water.

If extreme accuracy be necessary, after completing a determination, destroy the slight red tint by an excess of a soluble chloride, and repeat the estimation on a fresh quantity of the water in a similar flask placed by the side of the former. By comparing the contents of the flasks, the first tinge of red in the second flask may be detected with great accuracy. It is absolutely necessary that the liquor examined should not be acid, unless with carbonic acid, nor more than very slightly alkaline. It must also be colourless, or nearly so. These conditions are generally found in waters, but, if not, they may be brought about in most cases by rendering the liquid just alkaline with lime water (free from chlorine), passing carbonic anhydride to saturation, boiling, and filtering. The calcic carbonate has a powerful clarifying action, and the excess of alkali is exactly neutralized by the carbonic anhydride. If this is not successful, the water must he rendered alkaline, evaporated to dryness, and the residue gently heated to destroy organic matter. The chlorine may then be extracted with water, and estimated in the ordinary way, either gravimetrically or volumetrically.

11. Estimation of Hardness.

The following method, devised by the late Dr. Thomas Clark, of Aberdeen, is in general use; and from its ease, rapidity, and accuracy, is of great value.

Uniformity in conducting it is of great importance; especially, the titration of the soap solution, and the estimation of the hardness of waters, should be performed in precisely similar ways.

Measure 50 c.c. of the water into a well-stoppered bottle of about 250 c.c. capacity, shake briskly for a few seconds, and suck the air from the bottle by means of a glass tube, in order to remove any carbonic anhydride which may have been liberated from the water. Add standard soap solution (E. β.) from a burette, one c.c. at a time at first, and smaller quantities towards the end of the operation, shaking well after each addition, until a soft lather is obtained, which, if the bottle is placed at rest on its side, remains continuous over the whole surface for five minutes. The soap should not be added in larger quantities at a time, even when the volume required is approximately known.

When more than 16 c.c. of soap solution are required by 50 c.c. of the water, a less quantity (as 25 or 10 c.c.) of the latter should be taken, and made up to 50 c.c. with recently boiled distilled water, so that less than 16 c.c. of soap solution will suffice, and the number expressing the hardness of the diluted water multiplied by 2 or 5, as the case may be.

When the water contains much magnesium, which may be known by the lather having a peculiar curdy appearance, it should be diluted, if necessary, with distilled water, until less than 7 c.c. are required by 50 c.c.

The volume of standard soap solution required for 50 c.c. of the water being known, the weight of calcic carbonate ($Ca\,CO^3$) corresponding to this may be ascertained from the following table*:—

---

* The table is calculated from that originally constructed by Dr. Clark, which is as follows:—

Degree of Hardness.	Measures of Soap Solution.	Differences for the next 1° of hardness.
0° (Distilled water),	1·4	1·8
1	3·2	2·2
2	5·4	2·2
3	7·6	2·0
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	1·9
8	17·5	1·9
9	19·4	1·9
10	21·3	1·8
11	23·1	1·8
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	—

Each "measure" being 10 grains, the volume of water employed 1000 grains, and each "degree" 1 grain of calcic carbonate in a gallon.

If the old weights and measures, grains and gallons, be preferred, this table may be used, the process being exactly as above described, but 1000 grains of water taken instead of 50 c.c., and the soap solution measured in 10 grain measures instead of cubic centimetres. If the volume of soap solution used be found exactly in the second column of the table, the hardness will, of course, be that shown on the same line in the first column. But if it be not, deduct from it the next lower number in the second column, when the corresponding degree of hardness in the first column will give the integral part of the result; divide the remainder by the difference on the same line in the third column, and the quotient will give the fractional part. For example, if 1000 grains of water require 16 "measures" of soap, the calculation will be as follows:

16·0
— 15·6 (= 7° hardness).
(Difference =) 1·9) ·4
·21

therefore the hardness is 7·21 grains of $Ca\,CO^3$ per gallon. The water must be diluted if necessary, so that the quantity of soap required does not exceed 32 measures in ordinary waters, and 14 measures in water containing much magnesium.

TABLE 7.

Table of Hardness, Parts in 100,000.

Volume of Soap Solution.	Ca CO^3 ⅌ 100,000.	Volume of Soap Solution.	Ca CO^3 ⅌ 100,000.	Volume of Soap Solution.	Ca CO^3 ⅌ 100,000.	Volume of Soap Solution.	Ca CO^3 ⅌ 100,000.
c.c.		c.c.		c.c.		c.c.	
		4·0	4·57	8·0	10·30	12·0	16·43
		1	·71	1	·45	1	·59
		2	·86	2	·60	2	·75
		3	5·00	3	·75	3	·90
		4	·14	4	·90	4	17·06
		5	·29	5	11·05	5	·22
		6	·43	6	·20	6	·38
0·7	·00	7	·57	7	·35	7	·54
0·8	·16	8	·71	8	·50	8	·70
0·9	·32	9	·86	9	·65	9	·86
1·0	·48	5·0	6·00	9·0	·80	13·0	18·02
1	·63	1	·14	1	·95	1	·17
2	·79	2	·29	2	12·11	2	·33
3	·95	3	·43	3	·26	3	·49
4	1·11	4	·57	4	·41	4	·65
5	·27	5	·71	5	·56	5	·81
6	·43	6	·86	6	·71	6	·97
7	·56	7	7·00	7	·86	7	19·13
8	·69	8	·14	8	13·01	8	·29
9	·82	9	·29	9	·16	9	·44
2·0	·95	6·0	·43	10·0	·31	14·0	·60
1	2·08	1	·57	1	·46	1	·76
2	·21	2	·71	2	·61	2	·92
3	·34	3	·86	3	·76	3	20·08
4	·47	4	8·00	4	·91	4	·24
5	·60	5	·14	5	14·06	5	·40
6	·73	6	·29	6	·21	6	·56
7	·86	7	·43	7	·37	7	·71
8	·99	8	·57	8	·52	8	·87
9	3·12	9	·71	9	·68	9	21·03
3·0	·25	7·0	·86	11·0	·84	15·0	·19
1	·38	1	9·00	1	15·00	1	·35
2	·51	2	·14	2	·16	2	·51
3	·64	3	·29	3	·32	3	·68
4	·77	4	·43	4	·48	4	·85
5	·90	5	·57	5	·63	5	22·02
6	4·03	6	·71	6	·79	6	·18
7	·16	7	·86	7	·95	7	·35
8	·29	8	10·00	8	16·11	8	·52
3·9	·43	7·9	·15	11·9	·27	9	·69
						16·0	·86

When water containing calcic and magnesic carbonates, held in solution by carbonic acid, is boiled, carbonic anhydride is expelled and the carbonates precipitated. The hardness due to these is said to be *temporary*, whilst that due to sulphates, chlorides, etc., and to the amount of carbonates soluble in pure water (the last named being about three parts per 100,000), is called *permanent.*

To estimate permanent hardness, a known quantity of the water is boiled gently for half-an-hour in a flask, on the mouth of which stands a vertical glass tube, about 1 meter in length, and 5 m.m. internal diameter, having a bulb blown on its lower end, which rests on the mouth of the flask. This tube condenses and returns a large proportion of the water, which is driven off as steam. At the end of the boiling, the water should be allowed to cool, and the original weight made up by adding recently boiled distilled water.

Much trouble may be avoided by using flasks of about the same weight, and taking so much water in each as will make up the same uniform weight. Thus, if all the flasks employed weigh less than 50 gm. each, let each flask with its contents be made to weigh 200 gm.

After boiling and making up to the original weight, filter the water, and determine the hardness in the usual way. The hardness thus found, deducted from that of the unboiled water, will give the *temporary* hardness.

The quantities of the following substances which may be present in a sample of water are subject to such great variations that no definite directions can be given as to the volume of water to be used. The analyst must judge in each case from a preliminary experiment what will be a convenient quantity to take.

12. Sulphuric Acid.

Acidify a litre or less of the water with hydrochloric acid, concentrated on the water bath to about 100 c.c., and while still hot add a slight excess of baric chloride. Filter, wash, ignite, and weigh as baric sulphate, or estimate volumetrically as in § 40. Wildenstein's method described on page 97 gives exceedingly good results.

13. Hydric Sulphide.

Titrate with a standard solution of iodine in potassic iodide, with starch as an indicator as in § 32, details are further given in § 68. 3.

14. Phosphoric Acid.

Acidify a litre or more of the water with nitric acid, concentrate to a small bulk, and add a large excess of a solution of ammonic molybdate with a large proportion of nitric acid, § 69. *d.* Allow to stand for 12 hours in a warm place, filter, dissolve the precipitate in ammonia, precipitate with magnesia mixture, and weigh as magnesic pyrophosphate, or if the quantity is large, it may be estimated volumetrically, as in § 69. 2.

15. Silicic Acid.

Acidify a litre or more of the water with hydrochloric acid, evaporate, and dry the residue thoroughly. Then moisten with hydrochloric acid, dilute with hot water, and filter off, wash, ignite, and weigh the separated silica.

16. Iron.

To the filtrate from the estimation of silicic acid add a few drops of nitric acid, and concentrate to a small bulk; add excess of ammonia, and heat gently for a short time. Filter off the precipitate, and weigh as ferric oxide, or estimate the iron in the washed precipitate volumetrically, as in § 42. 7.

17. Calcium.

To the filtrate from the iron estimation add excess of ammonic oxalate, filter off the calcic oxalate, ignite and weigh as calcic carbonate, or estimate volumetrically with permanganate as in § 49.

18. Magnesium.

To the filtrate from the calcium estimation add sodic phosphate (or, if alkalies are to be determined in the filtrate, ammonic phosphate), and allow to stand for 12 hours in a warm place. Filter, ignite the precipitate, and weigh as magnesic pyrophosphate.

19. Potassium and Sodium.

These are generally determined jointly, and for this purpose the filtrate from the magnesium estimation may be used. Evaporate to dryness, and heat gently to expel ammonium salts, remove phos-

TABLE 8. **Results of Analysis expressed**

Number of Sample.	DESCRIPTION.	REMARKS.
	Upland Surface Waters.	
I.	The Dee above Balmoral, March 9th, 1872, ...	Clear ... ...
II.	Glasgow Water supply from Loch Katrine, May 18th, 1876	Clear; very pale br
III.	Liverpool Water supply from Rivington Pike, June 4th, 1869	Clear ... ...
IV.	Manchester Water supply, May 9th, 1874	Turbid ... ...
V.	Cardiff Water supply, Oct. 18th, 1872	Clear ... ...
	Surface Water from Cultivated Land.	
VI.	Dundee Water supply, March 12th, 1872	Turbid; brownish yel
VII.	Norwich Water supply, June 18th, 1872	Slightly turbid ...
	Shallow Wells.	
VIII.	Cirencester, Market Place, Nov. 4th, 1870	Slightly turbid ...
IX.	Marlborough, College Yard, Aug. 22nd, 1873	Clear ... ...
X.	Birmingham, Hurst Street, Sept. 18th, 1873	Clear; strong saline
XI.	Sheffield, Well near, Sept. 27th, 1870	Very turbid & offen- sive. Swarmin with bacteria, &c.
XII.	London, Aldgate Pump, June 5th, 1872	Clear ... ...
XIII.	London, Wellclose Square, June 5th, 1872	Slightly turbid; saline
XIV.	Leigh, Essex, Churchyard Well, Nov. 28th, 1871 ...	Slightly turbid ...
	Deep Wells.	
XV.	Birmingham, Short Heath Well, May 16th, 1873 ...	Clear ... ...
XVI.	Caterham, Water Works Well, Feb. 14th, 1873 ...	Clear ... ...
	Ditto, Softened (Water supply)	... ...
XVII.	London, Albert Hall, May, 1872	Slightly turbid ...
XVIII.	Gravesend, Railway Station, Jan. 17th, 1873	Clear ... ...
	Springs.	
XIX.	Dartmouth Water supply, Jan. 8th, 1873	Turbid ... ...
XX.	Grantham Water supply, July 11th, 1873	Clear ... ...
	London Water supply—average monthly analyses during seven years, 1869—75.	
XXI.	From the Thames	... ...
XXII.	From the Lea	... ...
XXIII.	From Deep Wells in the Chalk	... ...
	Average Composition of Unpolluted Water.	
XXIV.	Rain Water, ... 39 samples	... ...
XXV.	Upland Surface Water, ... 195 „	... ...
XXVI.	Deep Well Water, ... 157 „	... ...
XXVII.	Spring Water, ... 198 „	... ...
XXVIII.	Sea Water, ... 23 „	... ...
	Sewage.	
XXIX.	Average from 15 "Midden" Towns, 37 analyses ...	... ...
XXX.	Average from 16 "Water Closet" Towns, 50 analyses ...	... ...
XXXI.	Salford, Wooden Street Sewer, March 15th, 1869 ...	... ...
XXXII.	Merthyr Tydfil, average 10 a.m. to 5 p.m., Oct. 20th, 1871, (after treatment with lime)	... ...
XXXIII.	Ditto, Effluent Water	... ...

in parts per 100,000. **TABLE 8.**

Organic Carbon.	Organic Nitrogen.	Organic C : N	Nitrogen as Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Inorganic Nitrogen.	Total Combined Nitrogen.	Chlorine.	Hardness.		
								Temporary.	Permanent.	Total.
·132	·014	9·4	0	0	0	·014	·50	0	1·5	1·5
·124	·014	8·9	·001	·003	·004	·018	·76	—	—	·2
·210	·029	7·2	·002	0	·002	·031	1·53	·3	3·7	4·0
·132	·031	4·1	·002	0	·002	·033	·90	0	2·7	2·7
·212	·031	6·8	0	·034	·034	·065	1·40	7·1	12·9	20·0
·418	·059	7·1	·001	·081	·082	·141	1·75	0	6·0	6·0
·432	·080	5·4	·012	·036	·048	·128	3·10	21·3	5·3	26·6
·041	·008	5·1	0	·362	·362	·370	1·60	18·4	4·6	23·0
·049	·015	3·3	0	·613	·613	·628	1·90	15·6	10·1	25·7
·340	·105	3·2	·511	14·717	15·228	15·333	36·50	27·5	99·6	127·1
1·200	·126	9·5	·091	0	·091	·217	2·20	2·0	1·4	3·4
·144	·141	1·0	·181	6·851	7·032	7·173	12·85	37·1	40·0	77·1
·278	·087	3·2	0	25·840	25·840	25·927	34·60	26·7	164·3	191·0
·210	·065	3·2	0	5·047	5·047	5·112	13·75	14·3	45·7	60·0
·009	·004	2·2	0	·447	·447	·451	1·30	4·6	5·1	9·7
·028	·009	3·1	0	·021	·021	·030	1·55	15·2	6·0	21·2
·015	·003	5·0								4·4
·168	·042	4·0	·007	·066	·073	·115	15·10	3·4	2·2	5·6
·127	·029	4·4	·063	2·937	3·000	3·029	5·40	27·9	14·5	42·4
·060	·016	3·7	0	·330	·330	·346	2·45	1·6	10·0	11·6
·048	·018	2·7	0	·833	·833	·851	2·05	17·1	6·5	23·6
·201	·033	6·1	·001	·204	·205	·238	1·77	—	—	21·2
·135	·024	5·6	0	·199	·199	·223	1·79	—	—	21·3
·047	·012	3·9	0	·421	·421	·433	2·43	—	—	28·7
·070	·015	4·7	·024	·003	·027	·042	·22	—	—	·3
·322	·032	10·1	·002	·009	·011	·043	1·13	1·5	4·3	5·4
·061	·018	3·4	·010	·495	·505	·523	5·11	15·8	9·2	25·0
·056	·013	4·3	·001	·383	·384	·397	2·49	11·0	7·5	18·5
·278	·165	1·7	·005	·033	·038	·203	1975·6	48·9	748·0	796·9
								Suspended Matter.		
								Mineral.	Organic.	Total.
4·181	1·975	2·1	4·476	0	4·476	6·451	11·54	17·81	21·30	39·11
4·696	2·205	2·1	5·520	·003	5·523	7·728	10·66	24·18	20·51	44·69
11·012	7·634	1·4	5·468	0	5·468	13·102	20·50	18·88	26·44	45·32
1·282	·952	1·3	1·054	·052	1·106	2·058	5·25	7·88	6·56	14·44
·123	·031	4·0	·048	·300	·348	·379	2·60		Trace.	

phoric acid with plumbic acetate, and the excess of lead in the hot solution by ammonia and ammonic carbonate. Filter, evaporate to dryness, heat to expel ammonium salts, and weigh the alkalies as chlorides.

It is, however, generally less trouble to employ a separate portion of water. Add to a litre or less of the water enough pure baric chloride to precipitate the sulphuric acid, boil with pure milk of lime, filter, concentrate, and remove the excess of lime with ammonic carbonate and a little oxalate. Filter, evaporate, and weigh the alkaline chlorides in the filtrate. If the water contains but little sulphate, the baric chloride may be omitted, and a little ammonic chloride added to the solution of alkaline chlorides.

If potassium and sodium must each be estimated, separate them by means of platinic chloride; or, after weighing the mixed chlorides, determine the *chlorine* present in them, and calculate the amounts of potassium and sodium by the following formula:—Calculate all the chlorine present as potassic chloride; deduct this from the weight of the mixed chlorides, and call the difference *d*. Then as 16·1 : 58·5 : : *d* : NaCl present. See also § 37.

20. Lead.

May be estimated by the method proposed by the late Dr. W. A. Miller. Acidulate the water with two or three drops of acetic acid, and add $\frac{1}{10}$ of its bulk of saturated aqueous solution of sulphuretted hydrogen. Compare the colour thus produced in a convenient cylinder with that obtained with a known quantity of a standard solution of a lead salt, in a manner similar to that described for the estimation of iron or copper, § § 42, 7. 44, 9. The lead solution contains 0·1831 gm. of normal crystallized plumbic acetate in a litre of distilled water, and therefore each c.c. contains 0·0001 gm. of metallic lead.

21. Arsenic.

Add to half a litre or more of the water enough sodic hydrate, free from arsenic, to render it slightly alkaline, evaporate to dryness, and extract with a little concentrated hydrochloric acid. Introduce this solution into the generating flask of a small Marsh's apparatus, and pass the evolved hydrogen, first through a U-tube filled with pumice, moistened with plumbic acetate, and then through a piece of hard glass tube about 150 m.m. in length, and 3 m.m. in diameter (made by drawing out combustion tube). At about its middle, this tube is heated to redness for a length of about 20 m.m. by the flame of a small Bunsen burner, and here the arsenetted hydrogen is decomposed, arsenic being deposited as a mirror on the cold part of the tube. The mirror obtained after the gas has passed slowly for an hour is compared with a series of standard mirrors obtained in a similar way with known quantities of arsenic. Care must be taken to ascertain in each experiment that the hydrochloric acid, zinc, and whole apparatus is free from arsenic, by passing the hydrogen slowly through the heated tube before introducing the solution to be tested.

THE INTERPRETATION OF THE RESULTS OF ANALYSIS.

§ 78. The primary form of natural water is rain, the chief impurities in which are traces of organic matter, ammonia, and ammonic nitrate derived from the atmosphere. On reaching the ground it becomes more or less charged with the soluble constituents of the soil, such as calcic and magnesic carbonates, potassic and sodic chlorides and other salts, which are dissolved, some by a simple solvent action, others by the agency of carbonic acid in solution. Draining off from the land, it will speedily find its way to a stream which, in the earlier part of its course, will probably be free from pollution by animal matter, except that derived from any manure which may have been applied to the land on which the rain fell. Thus comparatively pure, it will furnish to the inhabitants on its banks, a supply of water which after use will be returned to the stream in the form of sewage charged with impurity derived from animal excreta, soap, household refuse, &c., the pollution being perhaps lessened by submitting the sewage to some purifying process such as irrigation of land, filtration, or clarification. The stream in its subsequent course to the sea will be in some measure purified by slow oxidation of the organic matter and by the absorbent action of vegetation, but not to any great extent. Some of the rain will not, however, go directly to a stream, but sink through the soil to a well. If this be shallow, it may be considered as merely a pit for the accumulation of drainage from the immediately surrounding soil which, as the well is in most cases close to a dwelling, will be almost inevitably charged with excretal and other refuse, so that the water when it reaches the well will be contaminated with soluble impurities thence derived, and with nitrites and nitrates resulting from their oxidation. After use the water from the well will, like the river water, form sewage, and find its way to a river, or again to the soil, according to circumstances.

In the case of a deep well from which the surface water is excluded, the conditions are different. The shaft will usually pass through an impervious stratum, so that the water entering it will not be derived from the rain which falls on the area immediately surrounding its mouth, but from that which falls on the outcrop of the pervious stratum below the impervious one just mentioned; and if this be uninhabited, the water of the well will probably be entirely free from organic impurity or products of decomposition; but even if the water be polluted at its source, still it must pass through a very extensive filter before it reaches the well, and its organic matter will probably be in great measure converted by oxidation into bodies in themselves innocuous.

This is very briefly the general history of natural waters, and the problem presented to the analyst is to ascertain, as far as possible, from the quality and quantity of the impurities present, the previous history of the water, and its present condition and fitness for the purpose for which it is to be used.

It is impossible to give any fixed rules by which the results obtained by the foregoing method of analysis should be interpreted. The analyst must form an independent opinion for each sample from a consideration of all the results he has obtained. Nevertheless, the following remarks, illustrated by reference to the examples given in the accompanying table, which may be considered as fairly typical, will probably be of service. *(See pages* 328 *and* 329.*)*

Total Solid Matter.

Waters which leave a large residue on evaporation are, as a rule, less suited for general domestic purposes than those which contain less matter in solution, and are unfit for many manufacturing purposes. The amount of residue is also of primary importance as regards the use of the water for steam boilers, as the quantity of incrustation produced will chiefly depend upon it. It may vary considerably, apart from any unnatural pollution of the water, as it depends principally on the nature of the soil through or over which the water passes. River water, when but slightly polluted, contains generally from 10 to 40 parts. Shallow well water varies greatly, containing from 30 to 150 parts, or even more, as in examples X and XIII, the proportion here depending less on the nature of the soil than on the original pollution of the water. Deep well water also varies considerably; it usually contains from 20 to 70 parts, but this range is frequently overstepped, the quantity depending largely upon the nature of the strata from which the water is obtained. Example XV, being in the New Red Sandstone, has a small proportion, but XVII and XVIII in the Chalk have a much larger quantity. Spring waters closely resemble those from deep wells. Sewage contains generally from 50 to 100 parts, but occasionally less and frequently much more, as in example XXXI. The total solid matter, as a rule, exceeds the sum of the constituents determined; the nitrogen as nitrates and nitrites being calculated as potassic nitrate, and the chlorine as sodic chloride; but occasionally this is not the case, owing, it is likely, to the presence of some of the calcium as calcic nitrate or chloride.

Organic Carbon or Nitrogen.

The existing condition of the sample, as far as organic contamination is concerned, must be inferred from the amount of these two constituents. In a good water, suitable for domestic supply, the former should not, under ordinary circumstances, exceed 0·2 and the latter 0·02 parts.

Waters from districts containing much peat are often coloured more or less brown, and contain an unusual quantity of organic carbon, but this peaty matter is probably innocuous unless the quantity be extreme. The large proportion of organic carbon and nitrogen given in the average for unpolluted upland surface water in Table 8 (XXV), is chiefly due to the fact that upland gathering grounds are very frequently peaty. The examples given (I to V) may be taken as fairly representative of the character of upland surface waters free from any large amount of peaty matter. In surface waters from cultivated areas the quantity of organic carbon and nitrogen is greater owing to increased density of population, the use of organic manures, &c., the proportion being about 0·25 to 0·3 part of organic carbon, and 0·04 to 0·05 part of organic nitrogen. The water from shallow wells varies so widely in its character that it is impossible to give any useful average. In many cases, as for example in XIII and XIV, the amount is comparatively small, although the original pollutions, as shown by the total inorganic nitrogen and the chlorine, was very large; the organic matter in these cases having been almost entirely destroyed by powerful oxidation. In VIII and IX the original pollution was slight, and oxidation being active the organic carbon and nitrogen have been reduced to extremely small quantities. On the other hand in XI the proportion of organic matter is enormous, the oxidizing action of the surrounding soil being utterly insufficient to deal with the pollution. The danger attending the use of shallow well waters, which contain when analysed very small quantities of organic matters, arises chiefly from the liability of the conditions to variation. Change of weather and many other circumstances may at any time prevent the purification of the water, which at the time of the analysis appeared to be efficient. Moreover, it is by no means certain, that an oxidizing action which would be sufficient to reduce the organic matter in a water to a very small proportion, would be equally competent to remove the specific poison of disease. Hence the greater the impurity of the source of a water the greater the risk attending its use.

In deep well waters the quantity of organic carbon and nitrogen also extends through a wide range but is generally low, the average being about 0·06 part carbon and 0·02 part nitrogen (XXVI). Here the conditions are usually very constant, and if surface drainage be excluded the source of the water is of less importance. Springs in this as in most other respects resemble deep wells; the water from them being generally, however, somewhat purer. In sewages great variations are met with. Sewage on the average contains about four parts of organic carbon and two parts of organic nitrogen (XXIX and XXX), but the range is very great. In the table, XXXI is a very strong sample and XXXII a weak one. The effluent water from land irrigated with sewage is usually analogous to water from shallow wells, and its quality varies greatly according to the conditions of the irrigation.

Ratio of Organic Carbon to Organic Nitrogen.

The ratio of the organic carbon to the organic nitrogen given in the seventh column of the table (which shows the fourth term of the proportion—organic nitrogen : organic carbon : : 1 : x), is of great importance as furnishing a valuable indication of the nature of the organic matter present. When this is of vegetable origin the ratio is very high, and when of animal origin very low. This statement must, however, be qualified, on account of the different effect of oxidation on animal and vegetable substances. It is found that when organic matter of vegetable origin, with a high ratio of carbon to nitrogen, is oxidized, it loses carbon more rapidly than nitrogen, so that the ratio is reduced. Thus unoxidized peaty waters exhibit a ratio varying from about 8 to 20 or even more, the average being about 12; whereas, the ratio in spring water originally containing peaty matter, varies from about 2 to 5, the average being about 3·2. When the organic matter is of animal origin the action is reversed, the ratio being increased by oxidation. In unpolluted upland surface waters the ratio varies from about 6 to 12, but in peaty waters it may amount to 20 or more. In surface water from cultivated land it ranges from about 4 to 10, averaging about 6. In water from shallow wells it varies from about 2 to 8 with an average of about 4, but instances beyond this range in both directions are very frequent. In water from deep wells and springs, the ratio varies from about 2 to 6 with an average of 4, being low on account probably, of the prolonged oxidation to which it has been subjected, which, as has been stated above, removes carbon more rapidly than nitrogen. In sea water this action reaches a maximum, the time being indefinitely prolonged, and the ratio is on the average about 1·7. This is probably complicated by the presence, in some cases, of multitudes of minute living organisms. In sewage the ratio ranges from about 1 to 3 with an average of about 2.

When in the case of a water containing much nitrogen as nitrates and nitrites, this ratio is unusually low, incomplete destruction of nitrates during the evaporation may be suspected, and the estimation should be repeated. To provide for this contingency, if a water contain any considerable quantity of ammonia, it is well, when commencing the evaporation in the first instance, to set aside a quantity sufficient for this repetition, adding to it the usual proportion of sulphurous acid.

Nitrogen as Ammonia.

The ammonia in natural waters is derived almost exclusively from animal contamination, and its quantity varies between very wide limits. In upland surface waters it seldom exceeds 0·008 part, the average being about 0·002 part. In water from cultivated land the average is about 0·005 and the range is greater, being from *nil* to 0·025 part or even more. In water from shallow wells the variation is so great that it would be useless to attempt to state an average, all proportions from *nil* to as much as 2·5 parts having been observed. In waters from deep wells a very considerable proportion is often found, amounting to 0·1 part or even more, the average being 0·01 part, and the variations considerable. In spring water it is seldom that more than 0·01 part of nitrogen as ammonia occurs, the average being only 0·001 part. Sewage usually contains from 2 to 6 parts, but occasionally as much as 9 or 10 parts, the average being about five. Ammonia is readily oxidized to nitrates and nitrites, and hence its presence, in considerable quantity, usually indicates the absence of oxidation, and is generally coincident with the presence of organic matter. That sometimes found in waters from very deep wells is, however, probably due to subsequent decomposition of nitrates.

Nitrogen as Nitrates and Nitrites.

Nitrates and nitrites are produced by the oxidation of nitrogenous organic matter, and almost always from animal matter. In upland surface waters the proportion varies from *nil* to 0·05 part or very rarely more, but the majority of samples contain none or mere traces (I to V), the average being about 0·009 part. In surface waters from cultivated land the quantity is much greater, varying from *nil*, which seldom occurs, to 1 part, the average being about 0·25 part. The proportion in shallow wells is usually much greater still, ranging from *nil*, which very rarely occurs, to as much as 25 parts. It would be probably useless to attempt to state an average, but quantities of from 2 to 5 parts occur most frequently. In water from deep wells the range is from *nil* to about 3 parts and occasionally more, the average being about 0·5 part. In spring water the range is about the same as in deep well water, but the average is somewhat lower.

It sometimes happens that, when the supply of atmospheric oxygen is deficient, the organic matter in water is oxidized at the expense of the nitrates present; and occasionally, if the quantities happen to be suitably proportioned, they are mutually destroyed, leaving no evidence of pollution. This reduction of nitrates often occurs in deep well water, as for example, in that from wells in the Chalk beneath London Clay, where the nitrates are often totally destroyed. In sewages, putrefaction speedily sets in, and during this condition the nitrates are rapidly destroyed, and so completely and uniformly that it is probably needless to attempt their estimation, except in sewages which are very weak, or for other special reasons abnormal. Out of a large number of samples only a very few have been found which contained any nitrates, and those only very small quantities.

Total Inorganic Nitrogen.

When organic matter is oxidized it is ultimately resolved into inorganic substances. Its carbon appears as carbonic acid, its hydrogen as water, and its nitrogen as ammonia, nitrous acid, or nitric acid; the last two combining with the bases always present in water to form nitrites and nitrates. The carbon and hydrogen are thus clearly beyond the reach of the analyst, but the nitrogen compounds as has been shown can be accurately determined, and furnish us with a means of estimating the amount of organic matter which was formerly present in the water, but which has already undergone decomposition.

The sum of the amounts of nitrogen found in these three forms constitutes then a distinct and valuable term in the analysis, the *organic* nitrogen relating to the *present*, and the total *inorganic* nitrogen to the *past* condition of the water. Since ammonia, nitrites, and nitrates are quite innocuous, the total inorganic nitrogen does not indicate *actual* evil like the organic nitrogen, but *potential* evil, as it is evident that the innocuous character of a water which contains much nitrogen in these forms depends wholly on the permanence of the conditions of temperature, aëration, filtration through soil, &c., which have broken up the original organic matter; if these should at any time fail, the *past* contamination would become *present*, the nitrogen appearing in the organic form, the water being loaded in all likelihood with putrescent and contagious matter.

In upland surface waters which have not been contaminated to any extent by animal pollution the total inorganic nitrogen rarely exceeds 0·03 part. In water from cultivated districts the amount is greater, ranging as high as 1 part, the average of a large number of samples being about 0·22 part. It is useless to attempt any generalisation for shallow wells, as the proportion depends upon local circumstances. The amount is usually large and may reach, as seen in Example XIII, the enormous quantity of twenty five parts per 100,000. Waters containing from one to five parts are very commonly met with. In water from deep wells and springs, quantities ranging up to 3·5 parts have been observed, the average on a large series of analyses being 0·5 part for deep wells and about 0·4 part for springs. It must be remembered that the conditions attending deep wells and springs are remarkably permanent, and the amount of filtration which the water undergoes before reaching the well itself, or issuing from the spring, is enormous. Meteorological changes here have either no effect, or one so small and slow as not to interfere with any purifying actions which may be taking place. All other sources of water, and especially shallow wells, are on the other hand subject to considerable changes, a sudden storm after drought will wash large quantities of polluting matter into the water-course, or dissolve the filth which has been concentrating in the pores of the soil during the dry season and carry it into the well. Small indications therefore of a polluted origin are very serious in surface waters and shallow well waters, but are of less moment in water from deep wells and springs in which the *present* character is of chief importance, since whatever degree of purification may be observed may usually be trusted as permanent. The term "total inorganic nitrogen," has been chosen chiefly because it is based on actual results of analysis without the introduction of any theory whatever. It will be seen that it corresponds very nearly with the term "previous sewage or animal contamination" which was introduced by Dr. Frankland, and which was employed in the second edition of this work. Perhaps few terms have been more wonderfully misunderstood and misrepresented than that phrase, and it is hoped that the new term will be less liable to misconception. It will be remembered that the "previous sewage contamination" of a water was calculated by multiplying the sum of the quantities of nitrogen present as ammonia, nitrates, and nitrites, by 10,000 and deducting 320 from the product, the number thus obtained representing the previous animal contamination of the water in terms of average filtered London sewage. It was purely conventional, for the proportion of organic nitrogen present in such sewage was assumed to be 10 parts per 100,000, whereas in the year 1857 it was 8·4 parts and in 1869 only 7 parts. The deduction of 320 was made to correct for the average amount of inorganic nitrogen in rain water, and this is omitted in calculating "total inorganic nitrogen" for the following reasons:—The quantity is small, and the variations in composition of rain water at different times and under different circumstances very considerable, and it appears to obscure the significance of the results of analysis of very pure waters to deduct from all the same fixed amount. As, too, the average amount of total inorganic nitrogen in unpolluted surface waters is only 0·011 part (XVII), it cannot be desirable to apply a correction amounting to nearly three times that average, and so place a water which contains 0·032 part of total inorganic nitrogen on the same level as one which contains no trace of any previous pollution.

Chlorine.

This is usually present as sodic chloride, but occasionally, as has been mentioned before, it is most likely as a calcic salt. It is derived, in some cases from the soil, but more usually from animal excreta (human urine contains about 500 parts per 100,000), and is therefore of considerable importance in forming a judgment as to the character of a water. Unpolluted river and spring waters usually contain less than one part; average town sewage about eleven parts. Shallow well water may contain any quantity from a mere trace up to fifty parts, or even more. Its amount is scarcely affected by any degree of filtration through soil; thus, the effluent water from land irrigated with sewage contains the same proportion of chlorine as the sewage, unless it has been diluted by subsoil water or concentrated by evaporation. Of course, attention should be given to the geological nature of the district from which the water comes, the distance from the sea or other source of chlorine, &c., in order to decide on the origin of the chlorine. Under ordinary circumstances, a water containing more than three or four parts of chlorine should be regarded with suspicion.

Hardness.

This is chiefly of importance as regards the use of the water for cleansing and manufacturing purposes, and for steam boilers. It is still a moot point as to whether hard or soft water is better as an article of food. The temporary hardness is often said to be that due to carbonates held in solution by carbonic acid, but this is not quite correct; for even after prolonged boiling, water will still retain about three parts of carbonate in solution, and therefore when the total hardness exceeds three parts, that amount should be deducted from the permanent hardness and added to the temporary, in order to get the quantity of carbonate in solution. But the term "temporary" hardness properly applies to the amount of hardness which may be removed by boiling, and hence, if the total hardness be less than three parts, there is usually no *temporary*. As the hardness depends chiefly on the nature of the soil through and over which the water passes, the variations in it are very great; that from igneous strata has least hardness, followed in approximate order by that from Metamorphic, Cambrian, Silurian and Devonian rocks, Millstone Grit, London Clay, Bagshot Beds, New Red Sandstone, Coal Measures, Mountain Limestone, Oolite, Chalk, Lias, and Dolomite, the average in the case of the first being 2·4 parts, and of the last 41 parts. As animal excreta contain a considerable quantity of lime, highly polluted waters are usually extremely hard. Water from shallow wells contains varying proportions up to nearly 200 parts of total hardness (XIII). No generalisation can be made as to the proportion of permanent to temporary hardness.

Suspended Matter.

This is of a less degree of importance than the matters hitherto considered. From a sanitary point of view it is of minor interest, because it may be in most cases readily and completely removed by filtration. Mineral suspended matter is, however, of considerable mechanical importance as regards the formation of impediments in the river bed by its gradual deposition, and as regards the choking of the sand filters in water works, and organic suspended matter is at times positively injurious and always favours the growth of minute organisms.

From the determinations which have been described, it is believed that a sound judgment as to the character of a water may be made, and the analyst should hardly be content with a less complete examination. If, however, from lack of time or other cause, so much cannot be done, a tolerably safe opinion may be formed, omitting the determination of total solid matter, and organic carbon and nitrogen. But it must not be forgotten that by so doing the inquiry is limited as regards organic impurity to the determination of that which was formerly present, but has already been converted into inorganic substances. If still less must suffice, the estimation of nitrogen as nitrates and nitrites may be omitted, its place being to a certain extent supplied by that of chlorine, but especial care must then be taken to ascertain the source of the latter by examination of the district. If it be in any degree of mineral origin, no opinion can be formed from it as to the likelihood of organic pollution. At best, so slight an examination must be of but little value, and considering the rapidity with which the nitrogen as nitrates can be determined by the indigo process, the saving of time would be very small.

General Considerations.

In judging of the character of a sample of water, due attention must of course be paid to the purpose for which it is proposed to be used. The analyst frequently has only to decide broadly whether the water is good or bad, as for example in cases of the domestic supply to isolated houses or of existing town supplies. Water which would be fairly well suited for the former might be very objectionable for the latter, where it would be required to a certain extent for manufacturing purposes. Water which would be dangerous for drinking or cooking may be used for certain kinds of cleansing operations; but it must not be forgotten that unless great care and watchfulness are exercised there is considerable danger of this restriction being neglected, and especially if the objectionable water is nearer at hand than the purer supply. It would for this reason, probably, be very unsafe to attempt a double supply on a large scale in a town even if the cost of a double service of mains, &c., were not prohibitive.

It is often required to decide between several proposed sources of supply, and here great care is necessary, especially if the differences between the samples are not great. If possible, samples should be examined at different seasons of the year; and care should be taken that they are collected as nearly as possible at the same time and in a normal condition. River waters should as a rule not be examined immediately after a heavy rain when they are in flood. A sudden rainfall after a dry season will often foul a river more than a much heavier and more prolonged downfall after average weather. Similarly the sewage discharged from a town at the beginning of a heavy rainstorm is usually extremely foul, the solid matter which has been accumulating on the sides of the sewers and in corners and recesses, being rapidly washed out by the increased stream.

The possibility of *improvement* in quality must also be considered. A turbid water may generally be rendered clear by filtration, and this will often also effect some slight reduction in the quantity of organic matter; but while somewhat rapid filtration through sand or similar material will usually remove all solid suspended matter, it is generally necessary to pass the water very slowly through a more efficient material to destroy any large proportion of the organic matter in solution. Very fine sand, animal charcoal, and spongy iron are all in use for this purpose. The supply of oxygen must not be neglected. If the water contains only a small quantity of organic matter and is well aërated, the quantity of oxygen in solution may be sufficient and the filtration may then be continuous; but in many instances this is not the case, and it is then necessary that the filtration should be intermittent, the water being allowed at intervals to drain off from the filtering material in order that the latter may be well aërated, after which it is again fit for work.

Softening water by Clark's process generally removes a large quantity of organic matter (*See* Table 8, XVI) from solution, it being carried down with the calcic carbonate precipitate.

It is evident that no very definite distinction can be drawn between deep and shallow wells. In the foregoing pages, deep wells generally mean such as are more than 100 feet deep, but there are many considerations which qualify this estimate. A deep well may be considered essentially as one the water in which has filtered through a considerable thickness of porous material, and whether the shaft of such a well is deep or shallow will depend on circumstances. If the shaft passes through a bed of clay or other impervious stratum, and the surface water above that is rigidly excluded, the well should be classed as "deep" even if the shaft is only a very few feet in depth, because the water in it must have passed for a considerable distance below the clay. On the other hand, however deep the shaft of the well, it must be considered as "shallow" if water can enter the shaft near the surface, or if large cracks or fissures give free passage for surface water through the rock in which the well is sunk. With these principles in view, the water from wells may often be improved. Every care should be taken to exclude surface water from deep wells; that is to say, all water from strata within about 100 feet from the surface or above the first impervious bed. In very deep wells which pass through several such beds, it is desirable to examine the water from each group of pervious strata as this often varies in quality, and if the supply is sufficient, exclude all but the best.

In shallow wells much may often be accomplished in a similar manner by making the upper part of the shaft water tight. It is also desirable that the surfare for some distance round the well should be puddled with clay, concreted, or otherwise rendered impervious, so as to increase the thickness of soil through which the water has to pass. Drains passing near the well should be if possible diverted, and of course cesspools should be either abolished; or, if that is impracticable, removed to as great a distance from the well as is possible, and in addition made perfectly water tight. Changes such as these tend to diminish the uncertainty of the conditions attending a shallow well, but in most cases such a source of supply should, if possible, be abandoned as dangerous at best.

Clark's Process for Softening Hard Water.

The patent right of this process having expired, the public are free to use it.

This method of softening consists in adding lime to the hard water. It is only applicable to water which owes its hardness entirely, or chiefly, to the calcic and magnesic carbonates held in solution by carbonic acid (*temporary hardness*). Water which owes its hardness to calcic or magnesic sulphate (*permanent hardness*) cannot be thus softened, but any water which softens on boiling for half-an-hour will be softened to an equal extent by Clark's process. The hard water derived from chalk, limestone, or oolite districts, is generally well adapted for this operation.

To soften 700 gallons of water, about one ounce of quicklime is required for each part of temporary hardness in 100,000 parts of water. The quantity of quicklime required is thoroughly slaked in a pailful of water. Stir up the milk of lime thus obtained and pour it immediately into the cistern containing at least 50 gallons of the water to be softened, taking care to leave in the pail any heavy sediment that may have settled to the bottom in the few seconds that intervened between the stirring and pouring. Fill the pail again with water, and stir and pour as before. The remainder of the 700 gallons of water must then be added, or allowed to run into the cistern from the supply pipe. If the rush of the water does not thoroughly mix the contents of the cistern, this must be accomplished by stirring with a suitable wooden paddle. The water will now appear very milky, owing to the precipitation of the chalk which it previously contained in solution, together with an equal quantity of chalk which is formed from the quicklime added.

After standing for three hours the water will be sufficiently clear to use for washing, but to render it clear enough for drinking at least twelve hours' settlement is required. This process not only softens water, but it removes to a great extent objectionable organic matter present

The proportion of lime to water may be more accurately adjusted during the running in of the hard water, by taking a little water from the cistern at intervals in a small white cup, and adding to it a drop or two of solution of nitrate of silver which will produce a yellow or brownish colouration as long as there is lime present in excess. As soon as this becomes very faint and just about to disappear the flow of water must be stopped.

METHODS OF WATER ANALYSIS WITHOUT GAS APPARATUS.

§ 79. THE foregoing methods of estimating the organic impurities in potable waters, though very comprehensive and reliable, yet possess the disadvantage of occupying a good deal of time, and necessitate the use of a complicated and expensive set of apparatus, which may not always be within the reach of the operator.

Nothing of a strictly reliable character as to the nature of the organic matter or its quantity can be gained from the use of standard permanganate solution, and the same remark applies to the loss on ignition of the residue, both of which have been in past time largely used.

The Albuminoid Ammonia process. We are indebted to Messrs. Wanklyn, Chapman, and Smith, for this well-known method of estimating the quantity of nitrogenous organic matter in water, which depends upon the conversion of the nitrogen in such organic matter into ammonia when distilled with an alkaline solution of potassic permanganate.

The authors have given the term "Albuminoid ammonia" to the NH^3 produced from nitrogenous matter by the action of the permanganate, doubtless because the first experiments made in the process were made with albumin; but the authors also proved that ammonia may be obtained in a similar way from a great variety of itrogenous organic substances, such as hippuric acid, narcotine, trychnine, morphine, creatine, gelatine, casein, &c. Unfortunately, owever, although the proportion of nitrogen yielded by any one ubstance when treated with boiling alkaline permanganate appears o be definite, yet different substances give different proportions of heir nitrogen. Thus hippuric acid and narcotine yield the whole, ut strychnine and morphine only one-half of their known proportion of nitrogen. Hence the value of the numerical results thus btained depends entirely on the assumption that the nitrogenous rganic matter in water is *uniform in its nature*, and the authors ay that in a river polluted mainly by sewage "the disintegrating nimal refuse would be pretty fairly measured by ten times the lbuminoid ammonia which it yields."

It is stated by the authors that the albuminoid ammonia from a really good drinking water should not exceed 0·008 parts in 100,000. The average of fifteen samples of Thames water supplied to London by the various Water Companies in 1867 was 0·0089, and in five samples supplied by the New River Company 0·0068 parts per 100,000,

The rapidity and simplicity of the operation are the chief merits of this process, and the information to be obtained from its performance may for some purposes be of considerable value; and even if the numerical results cannot be insisted upon, yet a *good* water could not be condemned by it, and a *bad* one ought certainly not escape it. One thing is clearly evident, namely, that in using this process it is advisable only to form an opinion as to the character of a water by taking the estimations of chlorine, mineral nitrogen, total solids, &c., into consideration, since the process has no power of giving the ratios between the organic carbon and nitrogen; and hence a water contaminated merely with peaty organic matter would be equally condemned with one in which the impurity was derived from animal sewage.

The method was first communicated to the Chemical Society in 1867 (Jour. Chem. Soc., N.S., vol. v., p. 591), and several editions of their treatise have since been published by Messrs. Wanklyn and Chapman, describing their general methods of examining water, to which the reader is referred. The only novelty, however, is the estimation of the so-called "albuminoid ammonia," through the agency of boiling alkaline permanganate.

1. Estimation of Free Ammonia.

This process is conducted precisely as described in § 77.3, and the residue may be used immediately afterward for the estimation of albuminoid ammonia if desired, or both processes may be conducted as described by Wanklyn and Chapman as follows:—

Half a litre of the water is measured into the retort with 10 c.c. of saturated solution of sodic carbonate, and a Bunsen's burner placed close under the bottom of the retort (almost touching it), and lighted full on; the distillation soon commences, and the distillate must be received in a tall cylinder holding about 150 c.c., and marked at 50 and 100 c.c. Three or four such cylinders are required at hand during the operation. When 50 c.c. have been distilled, the amount of free ammonia in it is estimated with Nessler solution, precisely as described at pages 291, 292, except that to the 50 c.c.—2 c.c. of solution are added and well stirred. If the proportion is large, it will be necessary to distil a further 50 or 100 c.c., but, generally speaking, the whole of the free NH^3 will come over in the first 100 or 150 c.c., but in any case the distillation should be continued until 50 c.c. of the distillate contain less than $\frac{1}{100}$ milligramme of NH^3, which is of course readily ascertained by means of the comparative effects obtained simultaneously upon known solutions of ammonia.

Mr. Wanklyn, in his last edition of instructions, has recommended the uniform plan of Nesslerizing only the first 50 c.c. for free ammonia, throwing away the 150 c.c. subsequently distilled and calculating that it contains one-third of the quantity found in the first 50 c.c.

2. Estimation of Albuminoid Ammonia.

To the contents of the retort left from the operation just described, are at once added through a clean funnel inserted into the tubulure of the retort 50 c.c. of the following solution:—

Potassic permanganate, . . .	8 gm.
Potassic hydrate, . . .	200 gm.
Distilled water, ...	One litre.

This liquid should be boiled for a short time when made to expel ammonia, and should be tested on a sample of pure water, § 76 (A. δ.) before use, then preserved in a stoppered bottle.

Having added this, resume the distillation, and estimate the ammonia as before until no more is evolved; generally speaking, it is sufficient to distil 150 c.c. after adding the above liquid, estimating the ammonia in each 50 c.c. The boiling is often very irregular, especially in bad waters, and if so it is advisable to introduce into the retort a few small pieces of freshly ignited pumice to moderate the bumping. It is also always advisable to incline the neck of the retort upward, so that the liquid carried up by spirting may be returned as previously mentioned; the rather as manganese compounds in particular, have a powerful effect upon the colour produced by the Nessler solution, greatly intensifying it, and thus vitiating the results. The amount of ammonia estimated by the Nessler test in this distillate is entered as albuminoid ammonia, and the total result of both distillations may be tabulated as follows :—

Half a litre taken.	Milligm. NH^3.
1. Distillate from Na CO^3 . .	100 c.c. = 0·015
2. Do. from permanganate .	100 c.c. = 0·035
Do. from " .	100 c.c. = 0·015

This particular water therefore contains, per litre—

Free ammonia, . . .	0·03 mgm.
Albuminoid do, . . .	0·10 mgm.

Milligrammes per litre are equivalent to parts per million.

If it be desired to state the results in parts per 100,000—it is written thus,—

Free ammonia, . . .	0·003
Albuminoid ditto, . . .	0·010

3. Nitrogen as Nitrates and Nitrites.

These may be accurately estimated as described at pages 316 to 320, or a very fair approximate estimation may be rapidly made by adding to 100 c.c. of the water contained in one of the cylinders used for estimation of ammonia 10 c.c. of solution of sodic hydrate (C. ζ.), and a small piece of aluminium sheet,—as soon as the latter is dissolved, Nessler solution may be added, and an idea of the quantity of nitrates and nitrites obtained. The same quantity of Nessler solution should also be added to 100 c.c. of the water without treatment with sodic hydrate and aluminium, in order to obtain a correction for the quantity of free NH^3 in the water. This method does not, however, answer for some waters, since they produce a deposit rather than a colour with the **Nessler** test. The indigo process described at pages 112 and 320 requires even less time and gives more accurate results. Professor T. E. **Thorpe's** method alluded to on page 104 is a very good one for the estimation of nitrates in waters; the most suitable apparatus for the purpose is described in Professor **Attfield's** Work on Pharmaceutical and General Chemistry, 6th edition.

4. Estimation of Total Solid Matter.

This may be done in either a platinum or glass vessel on a water bath (*See* page 316). The quantity to be taken for the estimation depends upon the nature of the water, and a fair judgment may be obtained from the appearance of the precipitate in the treatment with sodic carbonate in distilling for free ammonia, or from the hardness.

If only 70 or 100 c.c. are taken for evaporation as recommended by **Wanklyn**, extreme care and rapidity must be used in cooling and weighing the residue.

5. Estimation of Hardness.

This is performed exactly as described at page 323.

6. Colour and Smell of the Water.

A very tolerable opinion may be formed as to whether a sample of water contains unchanged organic matter by comparing its colour with that of distilled water; to this end, two white glass cylinders about 12 or 18 inches high, should be placed upon white paper or a white porcelain slab, one filled with distilled water and the other with the sample to be tested, side by side; any yellow or brown colour in the sample indicates the presence of organic matter, but it may not necessarily be owing to very objectionable impurity, since purely vegetable matter, such as peat, will often produce it.

The smell can be observed by shaking up some of the water in a large, wide-mouthed flask or bottle, and applying the nose to the bottle immediately afterwards. If the water be warmed to a slight extent, any objectionable smell is more readily detected. The estimation of chlorine, mineral constituents, metals, &c., may be made as described in the foregoing section or by other methods occurring in the previous parts of this book.

Continental chemists do not appear to have made water analysis a study so much as English or American chemists have, hence in the one chief German authority, "Untersuchung von Wasser" by Kubel and Tiemann, both the systems of Frankland, and Armstrong, and Wanklyn, Chapman, and Smith, are practically ignored; and the only methods recommended for estimating nitrogenous organic matter, are the old fashioned permanganate decolorising process, or the alkaline nitrate of silver method of Fleck; the estimation of mineral constituents of a harmless nature, sanitarily speaking, occupy the chief space in the treatise and hence are not worth reproducing here.

PART VII.

VOLUMETRIC ANALYSIS OF GASES.

Description of the necessary Apparatus, with Instructions for Preparing, Etching, Graduating, &c.

§ 80. This branch of chemical analysis, on account of its extreme accuracy, and in consequence of the possibility of its application to the analysis of carbonates, and of many other bodies from which gases may be obtained, deserves more attention than it has generally received, in this country at least. It will, therefore, be advisable to devote some considerable space to the consideration of the subject.

For a historical sketch of the progress of gas analysis, the reader is referred to Dr Frankland's article in the "Handwörterbuch der Chemie," and more complete details of the process than it will be necessary to give here will be found in that article, also in Bunsen's "Gasometry," and in Dr Russell's contributions to Watt's Chemical Dictionary.

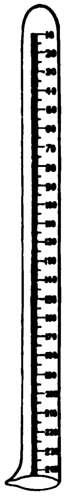


Fig. 43.

The apparatus employed by Bunsen, who was the first successfully to work out the processes of gas analysis, is very simple. Two tubes, the absorption tube and the eudiometer, are used, in which the measurement and analysis of the gases are performed. The first of these tubes is about 250 m.m. long and 20 m.m. in diameter, closed at one end, and with a lip at one side of the open extremity, to facilitate the transference of the gas from the absorption tube to the eudiometer (fig. 43). The eudiometer has a length of from 500 to 800 m.m., and a diameter of 20 m.m. Into the closed end two platinum wires are passed, so as to enable the operator to pass an electric spark through any gas which the tube may contain (fig. 44). The mode of sealing in the platinum wires is as follows:—When the end of the tube is closed, and while still hot, a finely-pointed blowpipe flame is directed against the side of the tube at the base of the hemispherical end. When the glass is soft, a piece of white-hot

um wire is pressed against it and rapidly drawn away. By
neans a small conical tube is produced. This operation is
repeated on the opposite side (fig. 45). One of the conical
is next cut off near to the eudiometer, so as to leave a small
(fig. 46), through which a piece of the moderately
latinum wire, reaching about two-thirds across the
is passed. The fine blowpipe flame is now brought
y on the wire at the point where it enters the tube,
ass rapidly fuses round the wire, making a perfectly
ht joint. If it should be observed that the tube
ny tendency to collapse during the heating, it will
essary to blow gently into the open end of the tube.
may be conveniently done by means of a long piece
outchouc connector, attached to the eudiometer,
enables the operator to watch the effect of the
ng more easily than if the mouth were applied
ly to the tube. When a perfect fusion of the glass
the wire has been effected, the point on the oppo-
ide is cut off and a second wire sealed in in the
manner (fig. 47). The end of the tube must be
d to cool very slowly; if proper attention is not
o this, fracture is very liable to ensue. When per-
cold, a piece of wood with a rounded end is passed
e eudiometer, and the two wires carefully pressed
t the end of the tube, so as to lie in contact with
ass, with a space of 1 or 2 m.m. between their points
8). It is for this purpose that the wires, when sealed
made to reach so far across the tube. The ends of
ires projecting outside the tube are then bent into
These loops must be carefully treated, for if fre-
ly bent they are very apt to break off close to the
besides this, the bending of the wire sometimes
a minute crack in the glass, which may spread and
ger the safety of the tube. These difficulties may
ercome by cutting off the wire close to the glass,
arefully smoothing the ends by rubbing them with
e of ground glass until they are level with the
e of the tube (fig. 49). In order to make contact with the
tion coil, a wooden American paper clip, lined with platinum
made to grasp the tube; the foil is connected with two
loops of platinum wire, and to these the wires from the coil

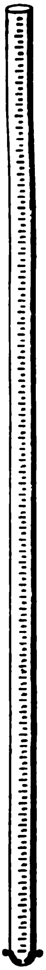


Fig. 44.

are attached (fig. 50). In this way no strain is put on the eudiometer wires by the weight of the wires from the coil, and perfect contact is ensured between the foil and platinum wires. It is also easy to clean the outside of the eudiometer without fear of injuring the instrument.

It will now be necessary to examine if the glass is perfectly fused to the wires. For this purpose the eudiometer is filled with mercury, inverted in the trough, the tube held in the hands, and brought with a rapid stroke against the bottom of the trough. This produces a momentary vacuum at the top of the tube; and if there is any leakage, small bubbles will be noticed arising from the junction of the glass with the wires. Of course this experiment

Fig. 45.

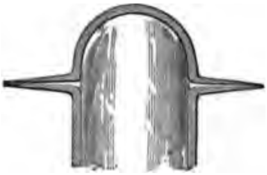
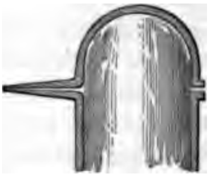


Fig. 46.



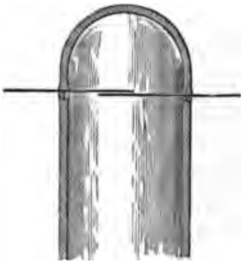


Fig. 47.

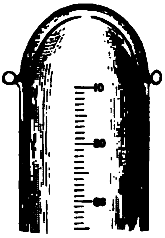


Fig. 48.

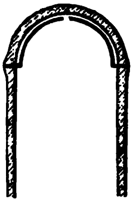


Fig. 49.

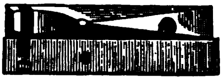


Fig. 50.

›e carefully performed; for if the shock is too violent, the y, on returning to the the tube, may break it.

tubes are graduated by ›llowing processes:—A ı fitted into the end of be, and a piece of stick, or anything that will a convenient handle, is into the cork. The tube ed over a charcoal fire or ›tion furnace, and coated nelted wax by means of ›l's hair brush. Some- . few drops of turpentine ixed with the wax to it less brittle, but this is ways necessary. If, on ;, it should be found that er of wax is not uniform, be may be placed in a dicular position before a l slowly rotated so as to evenly. The wax will e equally distributed on rface of the glass, the flowing off. The tube ›ot be raised to too high erature, or the wax may › too thin; but all thick should be avoided, as ay prove troublesome in ›sequent operation.

best and most accurate f marking the millimetre ns on the wax is by a ting machine, but the ısual process is to copy ›duations from another ı the following manner.

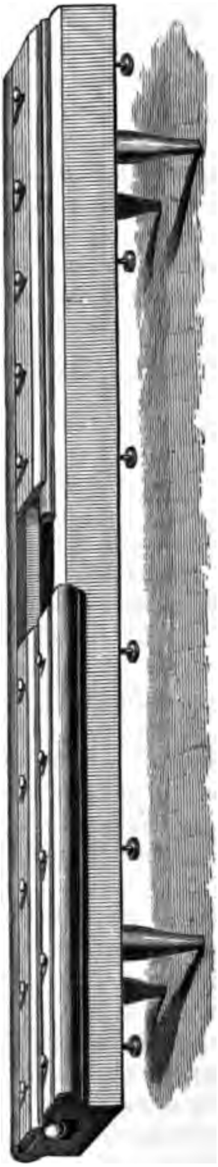


Fig. 51.

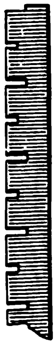


Fig. 52.

Fig. 53.

l glass tube, on which millimetre divisions l ıve already been deeply etched, is fixed in a groove in the graduating table, a straight edge of brass being screwed down on the tube and covering the ends of the lines. The standard tube is shown in the figure at the right hand end of the apparatus (fig. 51). The waxed tube is secured at the other end of the same groove, and above it are fixed two brass plates, one with a straight edge, and the other with notches at intervals of 5 m.m., the alternate notches being longer than the intermediate ones (fig. 52). A stout rod of wood, provided with a sharp steel point near one end, and a penknife blade at the other (fig. 53), is held so that the steel point rests in one of the divisions of the graduated tube, being gently pressed at the same time against the edge of the brass plate; the point of the knife blade is then moved by the operator's right hand across the portion of the waxed tube which lies exposed between the two brass plates. When the line has been scratched on the wax, the point is moved along the tube until it falls into the next division; another line is now scratched on the wax, and so on. At every fifth division the knife blade will enter the notches in the brass plate, making a longer line on the tube. After a little practice it will be found easy to do fifty or sixty divisions in a minute, and with perfect regularity. Before the tube is removed from the apparatus, it must be carefully examined to see if any mistake has been made. It may have happened that during the graduation the steel point slipped out of one of the divisions in the standard tube; if this has taken place, it will be found that the distance between the line made at that time and those on each side of it will not be equal, or a crooked or double line may have been produced. This is easily obliterated by touching the wax with a piece of heated platinum wire, after which another line is marked. The tube is now taken out of the table, and once more examined. If any portions of wax have been scraped off by the edges of the apparatus, or by the screws, the coating must be repaired with the hot platinum wire. Numbers have next to be marked opposite each tenth division, beginning from the closed end of the tube, the first division, which should be about 10 m.m. from the end, being marked 10 (see fig. 48). The figures may be well made with a steel pen. This has the advantage of producing a double line when the nib is pressed against the tube in making a down stroke. The date, the name of the maker of the tube, or its number, may now be written on the tube.

The etching by gaseous hydrofluoric acid is performed by supporting the tube by two pieces of wire over a long narrow leaden trough containing sulphuric acid and powdered fluor spar (fig. 54), and the whole covered with a cloth or sheet of paper. Of course it is necessary to leave the cork in the end of the tube to prevent the access of hydrofluoric acid to the interior, which might cause the tube to lose its transparency to a considerable extent. The time required for the action of the gas varies with the kind of glass employed: with ordinary flint glass, from ten minutes to half-an-hour is quite sufficient; if the leaden trough is heated the action may take place even still more rapidly. The tube is removed from time to time, and a small portion of the wax scraped off from a part of one of the lines, and if the division can be felt with the finger nail or the point of a knife, the operation is finished; if not, the wax must be replaced and the tube restored to the trough. When sufficiently etched the tube is washed with water, heated before a fire, and the wax wiped off with a warm cloth.

The etching may also be effected with liquid hydrofluoric acid, by applying it to the divisions on the waxed tube with a brush, or by placing the eudiometer in a gutta-percha tube closed at one end and containing some of the liquid.

Fig. 54.

As all glass tubes are liable to certain irregularities of diameter, it follows that equal lengths of a graduated glass tube will not contain exactly equal volumes, hence, it is, of course, impossible to obtain by measurement of length the capacity of the closed end of the tube.

In order to provide for this, the tube must be carefully calibrated. For this purpose it is supported vertically (fig. 55), and successive quantities of mercury poured in from a measure. This measure should contain about as much mercury as ten or twenty divisions of the eudiometer, and is made of a piece of thick glass tube, closed at one end, and with the edges of the open end ground perfectly flat. The tube is fixed into a piece of wood in order to avoid heating its contents during the manipulation. The measure may be filled with mercury from a vessel closed with a stop-cock terminating in a narrow vertical tube, which is passed to the bottom of the measure (fig. 56). On carefully opening the stopcock the mercury flows into the measure without leaving any air bubbles adhering to the sides. A glass plate is now pressed on the ground edges of the tube, which expels the excess of mercury and leaves the measure entirely filled. The mercury may be introduced into the measure in a manner which is simpler and as effectual, though perhaps not quite so convenient, by first closing it with a glass plate and depressing it in the mercurial trough, removing the plate from the tube, and again replacing it before raising the measure above the surface of the mercury. After pouring each measured quantity of mercury into the eudiometer, the air bubbles are carefully detached from the sides by means of a thin wooden rod or piece of whalebone, and the level of the mercury at the highest part of the curved surface carefully observed.

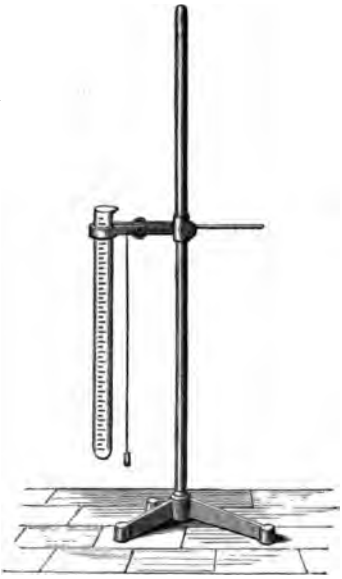


Fig. 55.

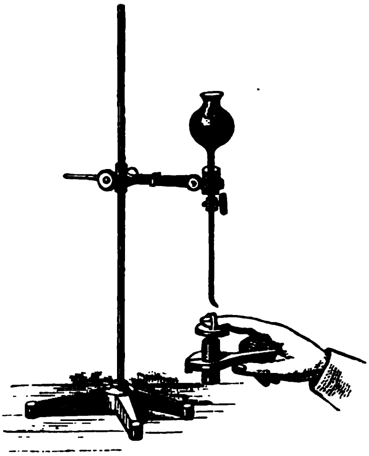


Fig. 56.

In all measurements in gas analysis it is, of course, essential that the eye should be exactly on a level with the surface of the mercury, for the parallax ensuing if this were not the case would produce grave errors in the readings. The placing of the eye in the proper position may be ensured in two ways. A small piece of looking-glass (the back of which is painted, or covered with paper to prevent the accidental soiling of the mercury in the trough), is placed behind, and in contact with the eudiometer. The head is now placed in such a position that the reflection of the pupil of the eye is precisely on a level with the surface of the mercury in the tube, and the measurement made. As this process necessitates the hand of the operator being placed near the eudiometer, which might cause the warming of the tube, it is preferable to read off with a telescope placed at the distance of from two to six feet from the eudiometer. The telescope is fixed on a stand in a horizontal position, and the support is made to slide on a vertical rod. The image of the surface of the mercury is brought to the centre of the field of the telescope, indicated by the cross wires in the eye-piece, and the reading taken. The telescope has the advantage of magnifying the graduations, and thus facilitating the estimation by the eye of tenths of the divisions. Fig. 57 represents the appearance of the tube and mercury as seen by an inverting telescope.

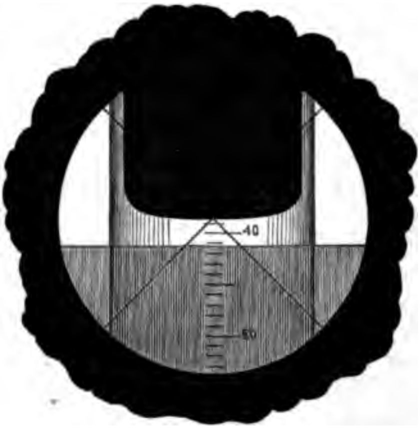


Fig. 57.

By this method the capacity of the tube at different parts of its length is determined. If the tube were of uniform bore, each measure of mercury would occupy the same length in the tube, but as this is never the case, the value of the divisions at all parts of the tube will not be found to be the same.

From the data obtained by measuring the space in the tube which is occupied by equal volumes of mercury, a table is constructed by which the comparative values of each millimetre of the tube can be found. The following results were obtained in the calibration of a short absorption eudiometer:—

On the introduction of the	3d	volume of mercury,	the reading was	12·8 m.m.
,, ,, ,,	4th	,,	,,	18·4
,, ,, ,,	5th	,,	,,	24·0
,, ,, ,,	6th	,,	,,	29·8
,, ,, ,,	7th	,,	,,	35·2
,, ,, ,,	8th	,,	,,	41·0

Thus, the standard volumes occupied 5·6 m.m., between 12·8 and 18·4
" " 5·6 " 18·4 " 24·0
" " 5·8 " 24·0 " 29·8
" " 5·4 " 29·8 " 35·2
" " 5·8 " 35·2 " 41·0

If we assume the measure of mercury to contain 5·8 volumes (the greatest difference between two consecutive readings on the tube), the volume at the six points above given will be as follows:—

At 12·8 it will be 17·4 or 5·8 × 3
18·4 " 23·2 " 5·8 × 4
24·0 " 29·0 " 5·8 × 5
29·8 " 34·8 " 5·8 × 6
35·2 " 40·6 " 5·8 × 7
41·0 " 46·4 " 5·8 × 8

Between the first and second readings these 5·8 volumes are contained in 5·6 divisions, consequently each millimetre corresponds to $\frac{5·8}{5·6} = 1·0357$ volumes. This is also the value of the divisions between the second and third readings. Between the third and fourth, 1 m.m. contains 1 vol.; between the fourth and fifth, 1 m.m. contains $\frac{5·8}{5·4} = 1·0741$ vol., and between the fifth and sixth m.m. = 1 vol.

From these data the value of each millimetre on the tube can readily be calculated. Thus 13 will contain the value of 12·8 + the value of 0·2 of a division at this part of the tube, or 17·4 + (1·0357 × 0·2) = 17·60714. There is, however, no need to go beyond the second place of decimals, and, for all practical purposes, the first place is sufficient. Thus, by adding or subtracting the necessary volumes from the experimental numbers, we find the values of the divisions nearest to the six points, at which the readings were taken, to be—

13 = 17·61 or 17·6
18 = 22·79 " 22·8
24 = 29·00 " 29·0
30 = 35·00 " 35·0
35 = 40·38 " 40·4
41 = 46·40 " 46·4

In a precisely similar manner the values of the intermediate divisions are calculated, and we thus obtain the following table:—

Readings.	Values.		Readings.	Values.		Readings.	Values.	
10	14·50	14·5	21	25·89	25·9	32	37·15	37·1
11	15·54	15·5	22	26·93	26·9	33	38·22	38·2
12	16·57	16·6	23	27·96	28·0	34	39·30	39·3
13	17·61	17·6	24	29·00	29·0	35	40·38	40·4
14	18·65	18·6	25	30·00	30·0	36	41·40	41·4
15	19·68	19·7	26	31·00	31·0	37	42·40	42·4
16	20·71	20·7	27	32·00	32·0	38	43·40	43·4
17	21·75	21·8	28	33·00	33·0	39	44·40	44·4
18	22·79	22·8	29	34·00	34·0	40	45·40	45·4
19	23·82	23·8	30	35·00	35·0	41	46·40	46·4
20	24·86	24·9	31	36·07	36·1	&c.	&c.	&c.

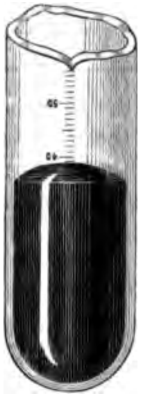
If it be desired to obtain the capacity of the tube in cubic centimetres, it is only necessary to determine the weight of the quantity of mercury the measure delivers, and the temperature at which the calibration was made, and to calculate the contents by the following formula:—

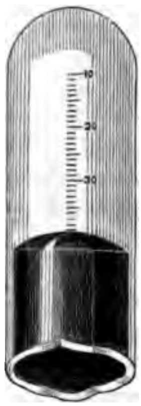
$$C = \frac{g \times (1 + 0{\cdot}0001815t)}{13{\cdot}596V}.$$

In which g represents the weight of the mercury contained in the measure, t the temperature at which the calibration is made, 0·0001815 being the coefficient of expansion of mercury for each degree centigrade, V the volume read off in the eudiometer, and C the number of cubic centimetres required.

A correction has to be made to every number in the table on account of the surface of the mercury assuming a convex form in the tube. During the calibration, the convexity of the mercury is turned towards the open end of the tube (fig. 58), whilst in the measurement of a gas the convexity will be in the opposite direction (fig. 59). It is obvious that the quantity of mercury measured during the calibration, while the eudiometer is inverted, will be less than a volume of gas contained in the tube when the mercury stands at the same division, while the eudiometer is erect. The necessary amount of correction is determined by observing the position of the top of the meniscus, and then introducing a few drops of a solution of corrosive sublimate, which will immediately cause the surface of the mercury to become horizontal (fig. 60), and again measuring.

It will be observed that in fig. 59 the top of the meniscus was at the division 39, whereas in fig. 60, after the addition of corrosive sublimate, the horizontal surface of the mercury stands at 38·7, giving a depression of 0·3 m.m. If the tube were now placed erect, and gas introduced so that the top of the meniscus was at 39, and if it were now possible to overcome the capillarity, the horizontal surface would stand at 39·3. The small cylinder of gas between 38·7 and 39·3, or 0·6 divisions, would thus escape measurement. This number 0·6 is therefore called the *error of meniscus*, and must be added to all readings of gas in the eudiometer. The difference, therefore, between the two readings is multiplied by two and the volume represented by the product obtained—the *error of meniscus*—is added to the measurements before finding the corresponding capacities by the table. In the case of the tube, of which the calibration is given above, the difference between the two readings was 0·4 m.m., making the error of meniscus 0·8.


* Fig. 58.


* Fig. 59.

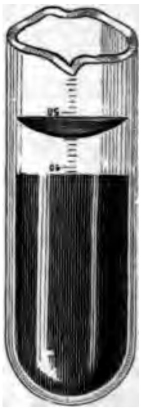


Fig. 60.

All experiments on gas analysis should be conducted in a room set apart for the purpose, with the window facing the north, so that the sun's rays cannot penetrate into it, and carefully protected from flues or any source of heat which might cause a change of temperature of the atmosphere. The mercury employed should be purified, as far as possible, from lead and tin, which may be done by leaving it in contact with dilute nitric acid in a shallow vessel for some time, or by keeping it when out of use under concentrated sulphuric acid to which some mercurous sulphate has been added. This mercury reservoir may conveniently be made of a glass globe with a neck at the top and a stopcock at the bottom (fig. 61), and which is not filled more than one-half, so as to maintain as large a surface as possible in contact with the sulphuric acid. Any foreign metals (with the exception of silver, gold, and platinum) which may be present are removed by the mercurous sulphate, an equivalent quantity of mercury being precipitated. This process, which was originated by M. Deville, has been in use for many years with very satisfactory results, the mercury being always clean and dry when drawn from the stopcock at the bottom of the globe. The mouth of the globe should be kept close to prevent the absorption of water by the sulphuric acid.

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* In these the mercury should just touch 39.

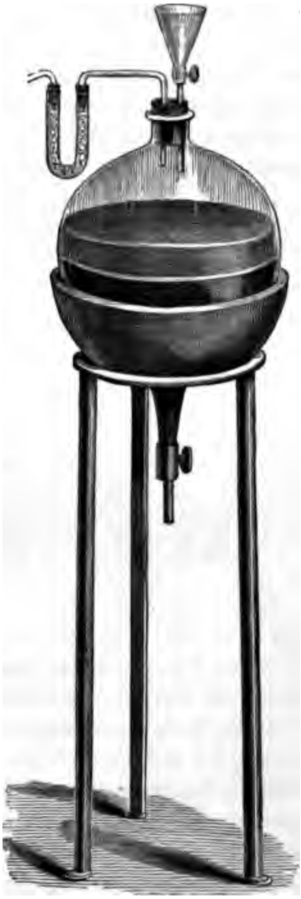

Fig. 61.

In all cases, where practicable, gases should be measured when completely saturated with aqueous vapour: to ensure this the top of the eudiometer and absorption tubes should be moistened before the introduction of the mercury. This may be done by dipping the end of a piece of iron wire into water and touching the interior of the closed extremity of the tube with the point of the wire.

In filling the eudiometer, the greatest care must of course be taken to exclude all air bubbles from the tubes. This may be effected in several ways: the eudiometer may be held in an inverted or inclined position, and the mercury introduced through a narrow glass tube which passes to the end of the eudiometer and communicates, with the intervention of a stopcock, with a reservoir of mercury (fig. 62). On carefully opening the stopcock, the mercury slowly flows into the eudiometer, entirely displacing the air. The same result may be obtained by placing the eudiometer nearly in a horizontal position, and carefully introducing the mercury from a test-tube without a rim (fig. 63). Any minute bubbles adhering to the side may generally be removed by closing the mouth of the tube with the thumb and allowing a small air bubble to rise in the tube, and thus to wash it out. After filling the eudiometer entirely with mercury, and inverting it over the trough, it will generally be found that the air bubbles have been removed.

For the introduction of the gases, the eudiometer should be placed in a slightly inclined position, being held by a support attached to

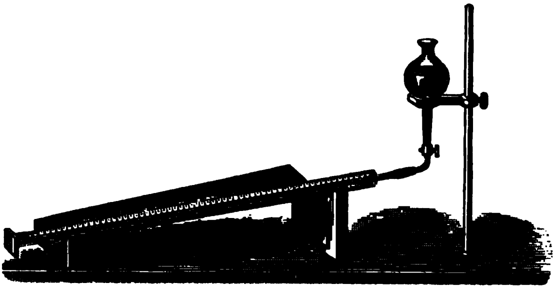

Fig. 62.

the mercurial trough (fig. 64), and the gas transferred from the tube in which it has been collected. The eudiometer is now put in an absolutely vertical position, determined by a plumb-line placed near it, and a thermometer suspended in close proximity. It must then be left for at least half-an-hour, no one being allowed to enter the room in the mean time. After the expiration of this period, the operator enters the room, and by means of the telescope placed several feet from the mercury table, carefully observes the height of the mercury in the tube, estimating the tenths of a division with the eye, which can readily be done after a little practice. He next reads the thermometer with the telescope, and finally the height of the mercury in the trough is read off on the tube, for which purpose the trough must have glass sides. The difference between these two numbers is the length of the column of mercury in the eudiometer, and has to be subtracted from the reading of the barometer. It only remains to take the height of the barometer. The most convenient form of instrument for gas analysis is the syphon barometer, with the divisions etched on the tube. This is placed on the mercury table, so that it may be read by the telescope immediately after the measurements in the eudiometer. There are two methods of numbering the divisions on the barometer: in one the zero point is at or near the bend of the tube, in which case the height of the lower column must be subtracted from that of the higher; in the other the zero is placed near the middle of the tube, so that the numbers have to be added to obtain the actual height. In cases of extreme accuracy, a correction must be made for the temperature of the barometer, which is determined by a thermometer suspended in the open limb of the instrument, and passing through a plug of cotton wool. Just before observing the height of the barometer, the bulb of the thermometer is depressed for a moment into the mercury in the open limb, thus causing a movement of the mercurial column, which overcomes any tendency that it may have to adhere to the glass.

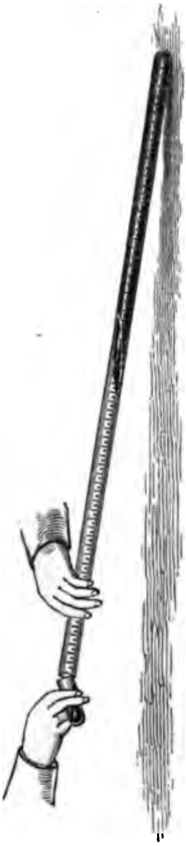

Fig. 63.

In every case the volume observed must be reduced to the normal temperature and pressure in order to render the results comparable. If the absolute volume is required, the normal pressure of 760 m.m. must be employed; but when comparative volumes only are desired, the pressure of 1000 m.m. is generally adopted, as it somewhat simplifies the calculation. In the following formula for correction of the volumes of gases:—

V^1 = the correct volume.

V = the volume found in the table, and corresponding to the observed height of the mercury in the eudiometer, the error of meniscus being of course included.

B = the height of the barometer (corrected for temperature if necessary) at the time of measurement.

b = the difference between the height of the mercury in the trough and in the eudiometer.

t = the temperature in centigrade degrees.

T = the tension of aqueous vapour in millimetres of mercury at $t°$ (see table at end of book). This number is, of course, only employed when the gas is saturated with moisture at the time of measurement.

Then

$$V^1 = \frac{V \times (B - b - T)}{760 \times (1 + 0{\cdot}003665t)},$$

when the pressure of 760 m.m. is considered the normal one; or,

$$V = \frac{V \times (B - b - T)}{1000 \times (1 + 0{\cdot}003665t)},$$

when the normal pressure of 1 metre is adopted.

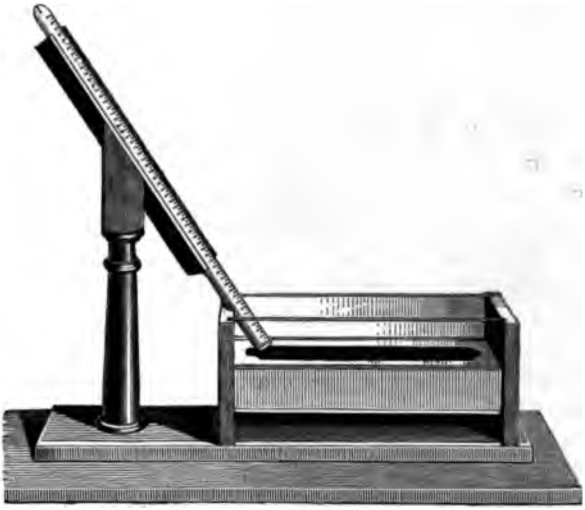

Fig. 64.

In cases where the temperature at measurement is below C° (which rarely happens), the factor $1 + 0{\cdot}003665t$, must be placed in the numerator.

Tables have been constructed containing the values of T; of $1 + 0{\cdot}003665t$ and of $760 \times (1 + 0{\cdot}003665t)$, which very much facilitate the numerous calculations required in this branch of analysis (see tables above mentioned).

We shall now be in a position to examine the methods employed in gas analysis. Some gases may be estimated directly; that is, they may be absorbed by certain re-agents, the diminution of the volume indicating the quantity of the gas present. Some are determined indirectly; that is, by exploding them with other gases, and measuring the quantities of the products. Some gases may be estimated either directly or indirectly, according to the circumstances under which they are found.

§ 81.

1. GASES ESTIMATED DIRECTLY.

A. Gases Absorbed by Crystallized Sodic Phosphate and Potassic Hydrate:—

Hydrochloric acid,
Hydrobromic acid,
Hydriodic acid.

B. Gases Absorbed by Potassic Hydrate, and not by Crystallised Sodic Phosphate:—

Carbonic anhydride,
Sulphurous anhydride,
Hydrosulphuric acid.

C. Gases Absorbed by neither Crystallised Sodic Phosphate nor Potassic Hydrate:—

Oxygen,
Nitric oxide,
Carbonic oxide,
Hydrocarbons of the composition $\mathrm{Cn\ H^2n}$,
Hydrocarbons of the formula $(\mathrm{Cn\ H^2n+1})^2$
Hydrocarbons of the formula, $\mathrm{Cn\ H^2n+2}$, except Marsh gas.

2. GASES ESTIMATED INDIRECTLY.

Hydrogen,
Carbonic oxide,
Marsh Gas,
Methyl,
Ethylic hydride,
Ethyl,
Propylic hydride,
Butylic hydride,
Nitrogen.

DIRECT ESTIMATIONS.

Group A, containing Hydrochloric, Hydrobromic, and Hydriodic Acids.

§ 82. In Bunsen's method the re-agents for absorption are generally used in the solid form, in the shape of bullets. To make the bullets of sodic phosphate, the end of a piece of platinum wire, of about one foot in length, is coiled up and fixed in the centre of a pistol-bullet mould; it is well to bend the handles of the mould, so that when it is closed the handles are in contact, and may be fastened together by a piece of copper wire (fig. 65). The usual practice is to place the platinum wire in the hole through which the mould is filled; but it is more convenient to file a small notch in one of the faces of the open mould, and place the wire in the notch before the mould is closed. In this manner the wire is not in the way during the casting, and it is subsequently more easy to trim the bullet. Some ordinary crystallized sodic phosphate is fused in a platinum crucible (or better, in a small piece of wide glass tube, closed at one end and with a spout at the other, and held by a copper wire handle), and poured into the bullet mould (fig. 66). When quite cold, the mould is first gently warmed in a gas flame, opened, and the bullet removed. If the warming of the mould is omitted, the bullet is frequently broken in consequence of its adhering to the metal. Some chemists recommend the use of sodic sulphate instead of phosphate, which may be made into balls by dipping the coiled end of a piece of platinum wire into the salt fused in its water of crystallization. On removing the wire, a small quantity of the salt will remain attached to the wire. When this has solidified, it is again introduced for a moment and a larger

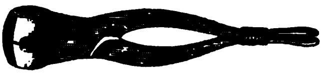

Fig. 65.

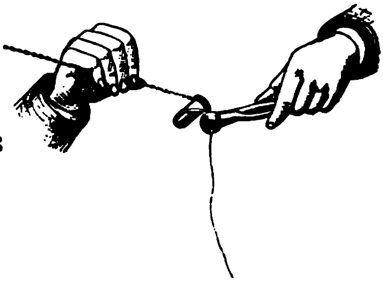

Fig. 66.

quantity will collect; and this is repeated until the ball is sufficiently large. The balls must be quite smooth, in order to prevent the introduction of any air into the eudiometer. When the bullets are made in a mould, it is necessary to remove the short cylinder which is produced by the orifice through which the fused salt has been poured.

In the estimation of these gases, it is necessary that they should be perfectly dry. This may be attained by introducing a bullet of fused calcic chloride. After the lapse of about an hour, the bullet may be removed, the absorption-tube placed in a vertical position, with thermometer, &c., arranged for the reading, and left for half-an-hour to assume the temperature of the air. When the reading has been taken, one of the bullets of sodic phosphate or sodic sulphate is depressed in the trough, wiped with the fingers while under the mercury in order to remove any air that it might have carried down with it, and introduced into the absorption-tube, which for this purpose is inclined and held in one hand while the bullet is passed into the tube with the other. Care must be taken that the whole of the platinum wire is covered with mercury while the bullet remains in the gas, otherwise there is a risk of air entering the tube between the mercury and the wire (fig. 67).

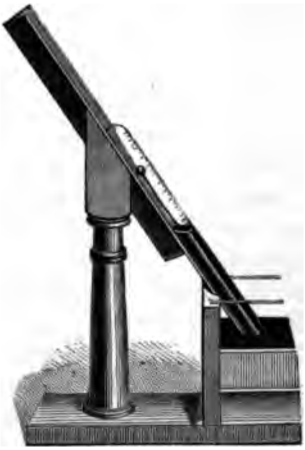

Fig. 67.

After standing for an hour, the bullet is withdrawn from the absorption-tube. This must be done with some precaution, so as to prevent any gas being removed from the tube. It is best done by drawing down the bullet by a brisk movement of the wire, the gas being detached from the bullet during the rapid descent of the latter into the mercury. The bullet may then be more slowly removed from the tube. As the sodic phosphate and sodic sulphate owe their absorbent powers for the gases to the water of crystallization they contain, the bullets must be preserved in a well-closed vessel, and care must be taken that the ball is not too small for the quantity of gas to be absorbed, as excess of the gas will cause the salt to deliquesce and soil the sides of the eudiometer. When the bullet has been removed, the gas must be dried as before with calcic chloride and again measured. If two or more of the gases are present in the mixture to be analysed, the sodic phosphate ball must be dissolved in water, and the chlorine, bromine, and iodine determined by the ordinary analytical methods. If this has to be done, care must be taken that the sodic phosphate employed is free from chlorine.

Group B. Gases absorbed by Potassic Hydrate, but not by Sodic Phosphate.

Carbonic anhydride, sulphuretted hydrogen, and sulphurous anhydride.

§ 83. If the gases occur singly, they are determined by means of a bullet of caustic potash made in the same manner as the sodic phosphate balls. The caustic potash employed should contain sufficient water to render the bullets so soft that they may be marked with the nail when cold. Before use the balls must be slightly moistened with water; and if large quantities of gas have to be absorbed, the bullet must be removed after some hours, washed with water, and returned to the absorption-tube. The absorption may extend over twelve or eighteen hours. In order to ascertain if it is completed, the potash ball is removed, washed, again introduced, and allowed to remain in contact with the gas for about an hour. If no diminution of volume is observed the operation is finished.

The following analyses of a mixture of air and carbonic anhydride will serve to show the mode of recording the observations and the methods of calculation required.

Analysis of a Mixture of Air and Carbonic Anhydride.

1. Gas Saturated with Moisture.

Height of mercury in trough = 171·8 m.m.
Height of mercury in absorption eudiometer . . . = 89·0 m.m.
Column of mercury in tube, to be subtracted from the height of barometer = b = 82·8 m.m.

Height of mercury in eudiometer = 82·0 m.m.
Correction for error of meniscus = 0·8 m.m.

Volume in table corresponding to 89·8 m.m. . . . $=V=$ 96·4
Temperature at which the reading was made . . . $=t=$ 12·2°
Height of barometer at time of observation . . . $=B=$765·25 m.m.
Tension of aqueous vapour at 12·2° $=T=$ 10·6 m.m.

$$V^1 = \frac{V \times (B-b-T)}{1000 \times (1 + 0{\cdot}003665t)} =$$

$$\frac{96{\cdot}4 \times (765{\cdot}25-82{\cdot}8-10{\cdot}6)}{1000 \times [1 + (0{\cdot}003665 \times 12{\cdot}2)]} =$$

$$\frac{96{\cdot}4 \times 671{\cdot}85}{1000 \times 1{\cdot}044713} = 61{\cdot}994$$

$$\begin{array}{rl} \log.\ 96{\cdot}4 = & 1{\cdot}98408 \\ \log.\ 671{\cdot}85 = & 2{\cdot}82727 \\ \hline & 4{\cdot}81135 \\ \log.\ (1000 \times 1{\cdot}044713) = & 3{\cdot}01900 \\ \hline & 1{\cdot}79235 = \log.\ 61{\cdot}994 = V^1 \end{array}$$

Corrected volume of air and $CO^2 = V^1 = 61{\cdot}994$.

After absorption of carbonic anhydride by bullet of potassic hydrate.

Gas Dry.

Height of mercury in trough = 172·0 m.m.
Height of mercury in absorption eudiometer . . . = 62·5 m.m.
Column of mercury in eudiometer $= b =$ 109·5 m.m.

Height of mercury in eudiometer = 62·5 m.m.
Correction for error of meniscus = 0·8 m.m.
63·3 m.m.

Volume in table corresponding to 63·3 m.m. . . . $=V=$ 69·35
Temperature . . . $=t=$ 10·8°
Barometer . . . $=B=$ 766·0 m.m.

$$V^1 = \frac{V \times (B - b)}{1000 \times (1 + 0{\cdot}003665t)} =$$

$$\frac{69{\cdot}35 \times (766{\cdot}0 - 109{\cdot}5)}{1000 \times [1 + (0{\cdot}003665 \times 10{\cdot}8)} =$$

$$\frac{69{\cdot}35 \times 656{\cdot}5}{1000 \times 1{\cdot}039582} = 43{\cdot}795$$

$$\begin{array}{rcl} \log.\ 69{\cdot}35 & = & 1{\cdot}84105 \\ \log.\ 656{\cdot}5 & = & \underline{2{\cdot}81723} \\ & & 4{\cdot}65828 \\ \log.\ (1000 \times 1{\cdot}039582) & = & \underline{3{\cdot}01686} \\ & & \underline{\underline{1{\cdot}64142}} = \log.\ 43{\cdot}795 = V^1 \end{array}$$

$$\begin{array}{lcl} \text{Corrected volume of air} & = & 43{\cdot}795 \\ \text{Air} + CO^2 & = & 61{\cdot}994 \\ \text{Air} & = & \underline{43{\cdot}795} \\ CO^2 & = & \underline{\underline{18{\cdot}199}} \end{array}$$

$$61{\cdot}994 : 18{\cdot}199 :: 100 : x = \text{percentage of } CO^2$$

$$x = \frac{18{\cdot}199 \times 100}{61{\cdot}995} = 29{\cdot}355$$

Percentage of CO^2 in mixture of air and gas = 29·355.

2. Gas Moist.

Height of mercury in trough = 174·0 m.m.
Height of mercury in eudiometer = 98·0 m.m.

Column of mercury in tube = b = 76·0 m.m.

Height of mercury in eudiometer = 98·0 m.m.
Correction for error of meniscus = 0·8 m.m.

98·8 m.m.

Volume in table, corresponding to 98·8 m.m. . . . = V = 105·6
Temperature . . . = t = 12·5°
Barometer . . . = B = 738·0 m.m.
Tension of aqueous vapour at 12·5° = T = 10·8 m.m.
Corrected volume of air and carbonic anhydride . . = 65·754

After absorption of CO^2.

Gas Dry.

Height of mercury in trough = 173·0 m.m.
Height of mercury in absorption eudiometer . . . = 70·3 m.m.
Column of mercury in tube = b = 102·7 m.m.
Height of mercury in eudiometer = 70·3 m.m.
Correction for error of meniscus = 0·8 m.m.
71·1 m.m.
Volume in table corresponding to 71·1 m.m. . . . = V = 77·4
Temperature . . = t = 14·1°
Barometer . . . = B = 733·5 m.m.

Corrected volume of air = 46·425
Air + CO^2 = 65·754
Air = 46·425
CO^2 = 19·329

65·754 : 19·329 : : 100 : 29·396.

	I.	II.
Percentage of CO^2 in mixture of air and gas	29·355	29·396

If either sulphurous anhydride, or sulphuretted hydrogen occurs together with carbonic anhydride, one of two modes of operation may be followed. Sulphuretted hydrogen and sulphurous anhydride are absorbed by manganic peroxide and by ferric oxide, which may be formed into bullets in the following manner. The oxides are made into a paste with water, and introduced into a bullet mould the interior of which has been oiled, and containing the coiled end of a piece of platinum wire, the mould is then placed on a sand bath till the ball is dry. The oxides will now be left in a porous condition which would be inadmissible for the purpose to which they are to be applied, the balls are therefore moistened several times with a syrupy solution of phosphoric acid, care being taken that they do not become too soft, so as to render it difficult to introduce them into the eudiometer. After the sulphuretted hydrogen or sulphurous anhydride has been removed, the gas should be dried by means of calcic chloride. The carbonic anhydride can now be determined by means of the bullet of potassic hydrate.

The second method is to absorb the two gases by means of a ball of potassic hydrate containing water, but not moistened on the exterior, then to dissolve the bullet in dilute acetic acid which has been previously boiled and allowed to cool without access of air, and to determine the amount of sulphuretted hydrogen or sulphurous anhydride by means of a standard solution of iodine. This process is especially applicable when rather small quantities of sulphuretted hydrogen have to be estimated.

Group C. This group contains the gases not absorbed by Potassic Hydrate or Sodic Phosphate, and consists of Oxygen, Nitric Oxide, Carbonic Oxide, Hydrocarbons of the formulæ $CnH^{2}n$ $(Cn^{2}H^{2}n+1)^{2}$, and $CnH^{2}n+{}^{2}$, except Marsh gas.

Oxygen was formerly determined by means of a ball of phosphorus, but it is difficult subsequently to free the gas from the phosphorous acid produced, and which exerts some tension and so vitiates the results, besides which, the presence of some gases interferes with the absorption of oxygen by phosphorus, and if any potassic hydrate remains on the side of the tube, from the previous absorption of carbonic anhydride, there is a possibility of the formation of phosphoretted hydrogen which would of course vitiate the analysis. A more convenient re-agent is a freshly prepared alkaline solution of potassic pyrogallate introduced into the gas in a bullet of papier maché. The balls of papier maché are made by macerating filter paper in water, and forcing as much of it as possible into a bullet mould into which the end of a piece of platinum wire has been introduced. In order to keep the mould from opening while it is being filled, it is well to tie the handles together with a piece of string or wire, and when charged it is placed on a sand-bath. After the mass is dry the mould may be opened, when a hard absorbent bullet will have been produced. The absorption of oxygen by the alkaline pyrogallate is not very rapid, and it may be necessary to remove the ball once or twice during the operation, and to charge it freshly.

Nitric oxide cannot be readily absorbed in an ordinary absorption tube, it may, however, be converted into nitrous anhydride and nitric peroxide by addition of excess of oxygen, absorbing the oxygen compounds with potassic hydrate and the excess of oxygen by potassic pyrogallate. The diminution of the volume will give the quantity of nitric oxide. This process is quite successful when the nitric oxide is mixed with olefiant gas and ethylic hydride, but it is possible that other hydrocarbons might be acted on by the nitrous compounds.

Carbonic oxide may be absorbed by two re-agents. If carbonic anhydride and oxygen be present they must be absorbed in the usual manner, and afterwards a papier maché ball saturated with a concentrated solution of cuprous chloride in dilute hydrochloric acid introduced. A ball of caustic potash is subsequently employed to remove the hydrochloric acid given off by the previous re-agent, and to dry the gas. Carbonic oxide may also be absorbed by introducing a ball of potassic hydrate, placing the absorption tube in a beaker of mercury, and heating the whole in a water-bath to 100° for 60 hours. The carbonic oxide is thus converted into potassic formate and entirely absorbed.

Olefiant Gas and other Hydrocarbons of the formula CnH^2n, are absorbed by Nordhausen sulphuric acid, to which an additional quantity of sulphuric anhydride has been added. Such an acid may be obtained by heating some Nordhausen acid in a retort connected with a receiver containing a small quantity of the same acid. This liquid is introduced into the gas by means of a dry coke bullet. These bullets are made by filling the mould, into which the usual platinum wire has been placed, with a mixture of equal weights of finely powdered coke and bituminous coal. The mould is then heated as rapidly as possible to a bright red heat, and opened after cooling; a hard porous ball will have been produced, which may be employed for many different re-agents. It is sometimes difficult to obtain the proper mixture of coal and coke, but when once prepared, the bullets may be made with the greatest ease and rapidity. The olefiant gas will be absorbed by the sulphuric acid in about an hour, though they may be left in contact for about two hours with advantage. If, on removing the bullet, it still fumes strongly in the air, it may be assumed that the absorption is complete. The gas now contains sulphurous, sulphuric, and perhaps carbonic anhydrides; these may be removed by a manganic peroxide ball, followed by one of potassic hydrate, or the former may be omitted, the caustic potash alone being used. The various members of the CnH^2n group cannot be separated directly, but by the indirect method of analysis their relative quantities in a mixture may be determined.

The hydrocarbons $(CnH^2n+{}^1)^2$ and $CnH^2n+{}^2$, may be absorbed by absolute alcohol, some of which is introduced into the absorption tube, and agitated for a short time with the gas. Correction has then to be made for the weight of the column of alcohol on the surface of the mercury, and for the tension of the alcohol vapour. This method only gives approximate results, and can only be employed in the presence of gases very slightly soluble in alcohol.

The time required in the different processes of absorption just described is considerable, perhaps it might be shortened by surrounding the absorption eudiometer with a wider tube, similar to the external tube of a Liebig's condenser, and through which a current of water is maintained; by means of a thermometer in the space between the tubes the temperature of the gas would be known, and the readings might be taken two or three minutes after the withdrawal of the re-agents. Besides this advantage, the great precaution necessary for maintaining a constant temperature in the room might be dispensed with. A few experiments made some years ago in this direction gave satisfactory results.

INDIRECT DETERMINATIONS.

§ 84. Gases which are not absorbed by any re-agents that are applicable in eudiometers over mercury, must be determined in an indirect manner, by exploding them with other gases, and noting either the change of volume or the quantity of their products of decomposition, or lastly, as is most frequently the case, by a combination of these two methods. Thus, for example, oxygen may be determined by exploding with excess of hydrogen, and observing the contraction; hydrogen may be estimated by exploding with excess of oxygen, and measuring the contraction; and marsh gas by exploding with oxygen, measuring the contraction, and also the quantity of carbonic anhydride generated.

The operation is conducted in the following manner:—The long eudiometer furnished with explosion wires is filled with mercury (after a drop of water has been placed at the top of the tube by means of an iron wire as before described), and some of the gas to be analysed is introduced from the absorption eudiometer. This gas is then measured with the usual precautions, and an excess of oxygen or hydrogen (as the case may be) introduced. These gases may be passed into the eudiometer directly from the apparatus in which they are prepared, or they may be previously collected in lipped tubes of the form of absorption tubes, so as to be always ready for use.

For the preparation of the oxygen a bulb is used which is blown at the closed end of a piece of combustion tube; the bulb is about half filled with dry powdered potassic chlorate, the neck drawn out, and bent to form a delivery tube. The chlorate is fused, and the gas allowed to escape for some time to ensure the expulsion of the atmospheric air; the end of the delivery tube is then brought under the orifice of the eudiometer, and the necessary quantity of gas admitted. When it is desired to prepare the oxygen beforehand, it may be collected directly from the bulb; or, another method to obtain the gas free from air, may be adopted by those who are provided with the necessary appliances; this is to connect a bulb containing potassic chlorate with a Sprengel's mercurial air-pump, and, after heating the chlorate to fusion, to produce a vacuum in the apparatus. The chlorate may be again heated until oxygen begins to pass through the mercury at the end of the Sprengel, the heat then withdrawn, and a vacuum again obtained. The chlorate is once more heated, and the oxygen collected at the bottom of the Sprengel. Of course the usual precautions for obtaining an air-tight joint between the bulb and the Sprengel must be taken, such as surrounding the caoutchouc connector with a tube filled with mercury.

The hydrogen for these experiments must be prepared by electrolysis, since that from other sources is liable to contamination with impurities which would vitiate the analysis. The apparatus employed by Bunsen for this purpose (fig. 68) consists of a glass tube, closed at the lower end, and with a funnel at the other, into which a delivery tube is ground, the funnel acting as a water joint; a platinum wire is sealed into the lower part of the tube, and near the upper end another wire, with a platinum plate attached, is fused into the glass. Some amalgam of zinc is

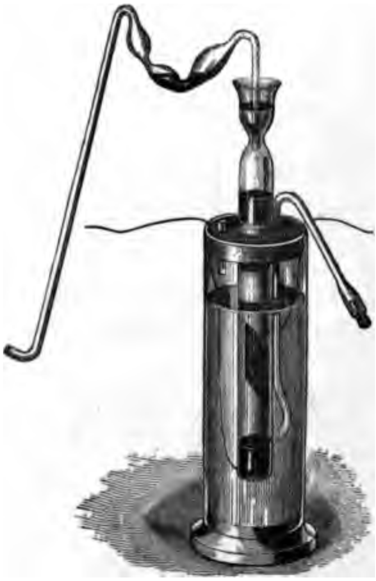

Fig. 68.

placed into the tube so as to cover the lower platinum wire, and the apparatus filled nearly to the neck with water, acidulated with sulphuric acid. On connecting the platinum wires with a battery of two or three cells, the upper wire being made the negative electrode, pure hydrogen is evolved from the platinum plate, and, after the expulsion of the air, may be at once passed into the eudiometer, or, if preferred, collected in tubes for future use. Unfortunately, in this form of apparatus, the zinc amalgam soon becomes covered with a saturated solution of zinc sulphate, which puts a stop to the electrolysis. In order to remove this layer, Bunsen has a tube fused into the apparatus at the surface of the amalgam; this is bent upwards parallel to the larger tube, and curved downwards just below the level of the funnel. The end of the tube is closed with a caoutchouc stopper. On removing the stopper, and pouring fresh acid into the funnel, the saturated liquid is expelled.

Another form of apparatus for preparing electrolytic hydrogen may readily be constructed. A six ounce wide mouth bottle is fitted with a good cork, or better, with a caoutchouc stopper. In the stopper four tubes are fitted (fig. 69): the first is a delivery tube, provided with a U tube, containing broken glass and sulphuric acid to conduct the hydrogen to the mercurial trough; the second tube, about 5 centimetres long, and filled with mercury, has fused into its lower end a piece of platinum wire carrying a strip of foil, or the wire may be simply flattened; the third tube passes nearly to the bottom of the bottle, the portion above the cork is bent twice at right angles, and cut off, so that the open end is a little above the level of the shoulder of the bottle, a piece of caoutchouc tube, closed by a compression cock, is fitted to the end of the tube; the fourth

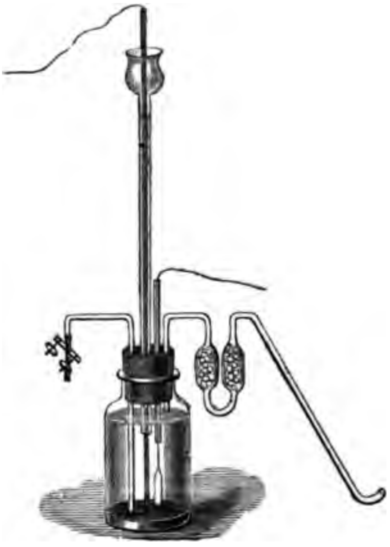

Fig. 69.

tube is a piece of combustion tube about 30 centimetres in length, and which may with advantage be formed into a funnel at the top. This tube reaches about one-third down the bottle, and inside it is placed a narrower glass tube attached at its lower end by a piece of caoutchouc connector to a rod of amalgamated zinc; the tube is filled with mercury to enable the operator readily to connect the zinc with the battery; some zinc amalgam is placed at the bottom of the bottle, and dilute sulphuric acid is poured in through the wide tube until the bottle is nearly filled with liquid. To use the apparatus, the delivery tube is dipped into mercury, the wire from the positive pole of the battery placed into the mercury in the tube to which the zinc is attached, and the negative pole connected by means of mercury with the platinum plate. The current, instead of passing between the amalgam at the bottom of the vessel and the platinum plate, as in Bunsen's apparatus, travels from the rod of amalgamated zinc to the platinum, consequently the current continues to pass until nearly the whole of the liquid in the bottle has become saturated with zinc sulphate. As soon as the hydrogen is evolved, of course a column of acid is raised in the funnel until the pressure is sufficient to force the gas through the mercury in which the delivery tube is placed. Care must be taken that the quantity of acid in the bottle is sufficient to prevent escape of gas through the funnel tube, and also that the delivery tube does not pass too deeply into the mercury so as to cause the overflow of the acid. When the acid is exhausted, the compression cock on the bent tube is opened and fresh acid poured into the funnel; the dense zinc sulphate solution is thus replaced by the lighter liquid, and the apparatus is again ready for use.

A very convenient apparatus for transferring oxygen and hydrogen into eudiometers is a gas pipette, figured and described, § 77, page 308.

It is necessary in all cases to add an excess of the oxygen or hydrogen before exploding, and it is well to be able to measure approximately the amount added without going through the whole of the calculations. This may be conveniently done by making a rough calibration of the eudiometer in the following manner:—The tube is filled with mercury, a volume of air introduced into it from a small tube, and the amount of the depression of the mercury noted; a second volume is now passed up, a further depression will be produced, but less in extent than the previous one, in consequence of the shorter column of mercury in the tube; this is repeated until the eudiometer is filled, and by means of a table constructed from these observations, but without taking any notice of the variations of thermometer or barometer, the operator can introduce the requisite quantity of gas. It may be convenient to make this calibration when the eudiometer is inclined in the support, and also when placed perpendicularly, so that the gas may be introduced when the tube is in either position. A table like the following is thus obtained:—

DIVISIONS.

Measures.	Tube Inclined.	Tube Perpendicular.
1	27	45
2	45	69
3	61	87
4	75	102
5	88	116
6	100	128
7	109	138
&c.	&c.	&c.

In explosions of hydrocarbons with oxygen, it is necessary to have a considerable excess of the latter gas in order to moderate the violence of the explosion. The same object may be attained by diluting the gas with atmospheric air, but it is found that sufficient oxygen serves equally well. If the gas contains nitrogen, it is necessary subsequently to explode the residual gas with hydrogen, and if oxygen only has been used for diluting the gas, a very large quantity of hydrogen must be added, which may augment the volume in the eudiometer to an inconvenient extent. When atmospheric air has been employed, this inconvenience is avoided. After the introduction of the oxygen, the eudiometer is restored to its vertical position, allowed to stand for an hour, and the volume read off.

The determination of the quantity of oxygen which must be added to combustible gases so as to prevent the explosion from being too violent, and at the same time to ensure complete combustion, has been made the subject of experiment. When the gases before explosion are under a pressure equal to about half that of the atmosphere, the following proportions of the gases must be employed:—

	Volume of Combustible Gas.	Volume of Oxygen.
Hydrogen,	1	1·5
Carbonic oxide,	1	1·5
Marsh gas,	1	5
Gases containing two atoms of carbon in the molecule, as Methyl, C^2H^6,	1	10
Gases containing three atoms of carbon in the molecule, as Propylic hydride, C^3H^8,	1	18
Gases containing four atoms of carbon in the molecule, as Ethyl, C^4H^{10},	1	25

In cases of mixtures of two or more combustible gases, proportionate quantities of oxygen must be introduced.

Fig. 70.

At the time of the explosion, it is necessary that the eudiometer should be carefully closed to prevent the loss of gas by the sudden expansion. For this purpose a thick plate of caoutchouc, 3 or 4 centimetres wide, is cemented on a piece of cork by means of marine glue, or some similar substance, and the lower surface of the cork cut so as to lie firmly at the bottom of the mercurial trough (fig. 70). It is, however, perferable to have the caoutchouc permanently fixed in the trough. As the mercury does not adhere to the caoutchouc, there is some risk of air entering the eudiometer after the explosion; this is obviated by rubbing the plate with some solution of corrosive sublimate before introducing it into the mercury, which causes the metal to wet the caoutchouc and remove all air from its surface. When the caoutchouc is not fixed in the trough, the treatment with corrosive sublimate has to be repeated before every experiment, and this soils the surface of the mercury to an inconvenient extent. The cushion

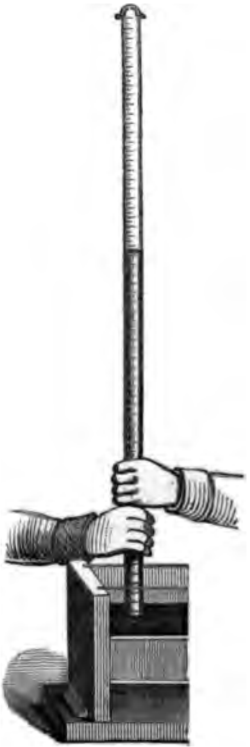

Fig. 71.

is next depressed to the bottom of the trough, and the eudiometer placed on it and firmly held down (fig. 71). If this is done with the hands, the tube must be held by that portion containing the mercury, for it is found that when eudiometers burst (which, however, only happens when some precaution has been neglected), they invariably give way just at the level of the mercury within the tube, and serious accidents might occur if the hands were at this point. The cause of the fracture at this point is the following:—Though the gas is at a pressure below that of the atmosphere before the explosion, yet at the instant of the passage of the spark, the expansion of the gas at the top of the tube condenses the layer just below it; this on exploding increases the density of the gas further down the tube, and by the time the ignition is communicated to the lowest quantity of gas, it may be at a pressure far above that of the atmosphere. It may be thought that the explosion is so instantaneous that this explanation is merely theoretical, but on exploding a long column of gas, the time required for the complete ignition is quite perceptible, and sometimes the flash may be observed to be more brilliant at the surface of the mercury. Some experimenters prefer to fix the eudiometer by means of an arm from a vertical stand, the arm being hollowed out on the under side, and the cavity lined with cork.

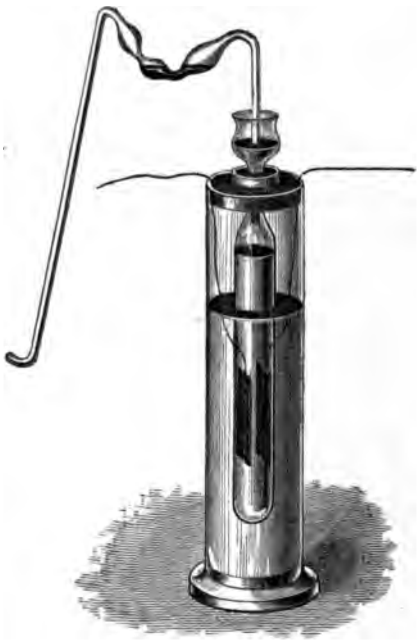

Fig. 72.

If a large quantity of incombustible gas is present, the inflammability of the mixture may be so much reduced that either the explosion does not take place at all, or, what may be worse, only a partial combustion ensues. To obviate this, some explosive mixture of oxygen and hydrogen, obtained by the electrolysis of water, must be introduced. The apparatus used by Bunsen for this purpose is shown in figure 72. The tube in which the electrolysis takes place is surrounded by a cylinder containing alcohol in order to prevent the heating of the liquid. A convenient apparatus for the preparation of this gas is made by blowing a bulb of about 4 centimetres in diameter on the end of a piece of narrow glass tube, sealing two pieces of flattened platinum wire into opposite sides of the globe, and bending the tube so as to form a delivery tube. Dilute sulphuric acid, containing about 1 volume of acid to 20 of water is introduced into the globe, either before bending the tube, by means of a funnel with a fine and long stem, or, after the bending, by warming the apparatus and plunging the tube into the acid. Care must be taken that the acid is dilute, and that the battery is not too strong, in order to avoid the formation of ozone, which would attack the mercury, causing the sides of the eudiometer to be soiled, at the same time producing a gas too rich in hydrogen.

The spark necessary to effect the explosion may be obtained from several sources. An ordinary electrical machine or electrophorus may be used, but these are liable to get out of order by damp. Bunsen uses a porcelain tube, which is rubbed with a silk rubber, coated with electrical amalgam; by means of this a small Leyden jar is charged. A still more convenient apparatus is an induction coil large enough to produce a spark of half an inch in length.

After the explosion the eudiometer is slightly raised from the caoutchouc plate to allow the entrance of mercury. When no more mercury rushes in, the tube is removed from the caoutchouc plate, placed in a perpendicular position, and allowed to remain for at least an hour before reading. After measuring the contraction, it is generally necessary to absorb the carbonic anhydride formed by the combustion by means of a potash ball in the way previously described. In some rare instances the amount of water produced in the explosion with oxygen must be measured. If this has to be done, the eudiometer, the mercury, the original gas, and the oxygen, must all be carefully dried. After the explosion the eudiometer is transferred to a circular glass vessel containing mercury, and attached to an iron wire support, by which the entire arrangement can be suspended in a glass tube adapted to the top of an iron boiler, from which a rapid current of steam may be passed through the glass tube so as to heat the eudiometer and mercury to a uniform temperature of 100°. From the measurements obtained at this temperature the amount of water produced may be calculated. If three combustible gases are present, the only data required for calculation are, the original volume of the gas, the contraction on explosion, and the amount of carbonic anhydride generated. When the original gas contains nitrogen, the residue after explosion with excess of oxygen consists of a mixture of oxygen and nitrogen. To this an excess of hydrogen is added, and the mixture exploded; the contraction thus produced divided by 3 gives the amount of oxygen in the residual gas, and the nitrogen is found by difference.

It is obvious that, by subtracting the quantity of residual oxygen, thus determined by explosion with hydrogen, from the amount added, in the first instance, to the combustible gas, the volume of oxygen consumed in the explosion may be obtained. Some chemists prefer to employ this number instead of the contraction as one of the data for the calculation.

We must now glance at the mode of calculation to be employed for obtaining the percentage composition of a gas from the numbers arrived at by the experimental observations.

The following table shows the relations existing between the volume of the more important combustible gases and the products of the explosion:—

Name of Gas.	Volume of Combustible Gas.	Volume of Oxygen Consumed.	Contraction after Explosion.	Volume of Carbonic Anhydride produced.
Hydrogen, H,	1	0·5	1·5	0
Carbonic Oxide, CO,	1	0·5	0·5	1
Methylic Hydride, CH^3H,	1	2	2	1
Acetylene, C^2H^2,	1	2·5	1·5	2
Olefiant Gas, C^2H^4,	1	3	2	2
Methyl, CH^3, CH^3,	1	3·5	2·5	2
Ethylic Hydride, C^2H^5H,	1	3·5	2·5	2
Propylene, C^3H^6,	1	4·5	2·5	3
Propylic Hydride, C^3H^7H,	1	5	3	3
Butylene, C^4H^8,	1	6	3	4
Ethyl, C^2H^5, C^2H^5,	1	6·5	3·5	4
Butylic Hydride, C^4H^9H,	1	6·5	3·5	4

As an example, we may take a mixture of hydrogen, carbonic oxide, and marsh gas, which gases may be designated by x, y, and z respectively. The original volume of gas may be represented by

A, the contraction by C, and the amount of carbonic anhydride by D.

A will, of course, be made up of the three components, or

$$A = x + y + z.$$

C will be composed as follows: When a mixture of hydrogen and oxygen is exploded, the gas entirely disappears. One volume of hydrogen combining with $\frac{1}{2}$ a volume of oxygen, the contraction will be $1\frac{1}{2}$ times the quantity of hydrogen present, or $1\frac{1}{2}x$. In the case of carbonic oxide, 1 volume of this gas uniting with half its volume of oxygen produces 1 volume of carbonic anhydride, so the contraction due to the carbonic will be $\frac{1}{2}$ its volume, or $\frac{1}{2}y$. Lastly, 1 volume of marsh gas combining with 2 volumes of oxygen generates 1 volume of carbonic anhydride, so the contraction in this case will be twice its volume, or $2z$. Thus we have—

$$C = 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z.$$

Since carbonic oxide on combustion forms its own volume of carbonic anhydride, the amount produced by the quantity present in the mixture will be y. Marsh gas also generates its own volume of carbonic anhydride, so the quantity corresponding to the marsh gas in the mixture will be z. Therefore

$$D = y + z.$$

It now remains to calculate the values of x, y, and z from the experimental numbers A, C, and D, which is done by the help of the following equations:—

$$\begin{aligned} A &= x + y + z\,, \\ C &= 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z\,, \\ D &= y + z\,. \end{aligned}$$

To find x—

$$\begin{array}{rcl} x + y + z &=& A\,, \\ y + z &=& D\,, \\ \hline x \qquad &=& A - D\,. \end{array}$$

For y we have—

$$\begin{array}{rcl} 4y + 4z &=& 4D\,, \\ 3x + y + 4z &=& 2C\,, \\ \hline -3x + 3y \qquad &=& 4D - 2C\,, \\ 3x \qquad\qquad &=& 3A - 3D\,, \\ \hline 3y \qquad &=& 3A - 2C + D\,, \quad \text{or} \end{array}$$

$$y = \frac{3A - 2C + D}{3}.$$

The value of z is thus found—

$$D = y + z \;\therefore$$
$$z = D - y =$$
$$D - \frac{3A - 2C + D}{3}, \quad \text{or}$$
$$\underline{z = \frac{2C - 3A + 2D}{3}}.$$

By replacing the letters A, C, and D by the numbers obtained by experiment, the quantities of the three constituents in the volume A may easily be calculated by the three formulæ:—

$$x = A - D \qquad = \text{hydrogen},$$
$$y = \frac{3A - 2C + D}{3} \qquad = \text{carbonic oxide},$$
$$z = \frac{2C - 3A + 2D}{3} \qquad = \text{marsh gas}.$$

The percentage composition is, of course, obtained by the simple proportions—

$A : x :: 100 :$ % of hydrogen ,
$A : y :: 100 :$ % of carbonic oxide ,
$A : z :: 100 :$ % of marsh gas.

If the gas had contained nitrogen, it would have been determined by exploding the residual gas, after the removal of the carbonic anhydride, with excess of hydrogen. The contraction observed, divided by 3, would give the volume of oxygen in the residue, and this, deducted from the residue, would give the amount of nitrogen. If A again represents the original gas, and n the amount of nitrogen it contains, the expression $A - n$ would have to be substituted, for A in the above equations.

It may be as well to develope the formula for obtaining the same results by observing the volume of oxygen consumed instead of the contraction. If B represent the quantity of oxygen, we shall have

$$B = \tfrac{1}{2}x + \tfrac{1}{2}y + 2z,$$

the values of A and D remaining as before, $x = A - D$.

z is thus found—

$$x + y + 4z = 2B,$$
$$\underline{x + y + z = A},$$
$$3z = 2B - A, \quad \text{or}$$
$$\underline{z = \frac{2B - A}{3}}.$$

For y—

$$D = y + z$$
$$y = D - z = D - \frac{2B - A}{3}, \text{ or}$$
$$y = \frac{3D - 2B + A}{3}$$

Thus we have—

$$x = A - D$$
$$y = \frac{3D - 2B + A}{3}$$
$$z = \frac{2B - A}{3}$$

Having thus shown the mode of calculation of the formulæ, it will be well to give some examples of the formulæ employed in some of the cases which most frequently present themselves in gas analysis. In all cases—

A = original mixture ,
C = contraction ,
D = carbonic anhydride produced.

1. Hydrogen and Nitrogen.

$$H = x;\ N = y.$$

Excess of oxygen is added, and the contraction on explosion observed :—

$$x = \frac{2C}{3},$$
$$y = \frac{3A - 2C}{3}, \text{ or } A - x.$$

2. Carbonic Oxide and Nitrogen.

$$CO = x;\ N = y.$$

The gas is exploded with excess of oxygen, and the amount of carbonic anhydride produced is estimated :—

$$x = D,$$
$$y = A - D.$$

3. Hydrogen, Carbonic Oxide, and Nitrogen.

$$H=x;\ CO=y;\ N=z.$$

In this case the contraction and the quantity of carbonic anhydride are measured:—

$$x=\frac{2C-D}{3},$$

$$y=D,$$

$$z=\frac{3A-2C-2D}{3}.$$

4. Hydrogen, Marsh Gas, and Nitrogen.

$$H=x;\ CH^4=y;\ N=z.$$

$$x=\frac{2C-4D}{3},$$

$$y=D,$$

$$z=\frac{3A-2C+D}{3}.$$

5. Carbonic Oxide, Marsh Gas, and Nitrogen.

$$CO=x;\ CH^4=y;\ N=z.$$

$$x=\frac{4D-2C}{3},$$

$$y=\frac{2C-D}{3},$$

$$z=A-D.$$

6. Hydrogen, Methyl (or Ethylic Hydride), and Nitrogen.

$$H=x;\ C^2H^6=y;\ N=z.$$

$$x=\frac{4C-5D}{6},$$

$$y=\frac{D}{2},$$

$$z=\frac{3A-2C+D}{3}.$$

7. Carbonic Oxide, Methyl (or Ethylic Hydride) and Nitrogen.

$CO=x;\ C^2H^6=y;\ N=z.$

$$x=\frac{5D-4C}{3},$$

$$y=\frac{2C-D}{3},$$

$$z=\frac{3A-4D+2C}{3}.$$

8. Hydrogen, Carbonic Oxide, and Marsh Gas.

$H=x;\ CO=y;\ CH^4=z.$

$$x=A-D,$$

$$y=\frac{3A-2C+D}{3},$$

$$z=\frac{2C-3A+2D}{3}.$$

9. Hydrogen, Carbonic Oxide, and Ethylic Hydride (or Methyl).

$H=x;\ CO=y;\ C^2H^6=z.$

$$x=\frac{3A+2C-4D}{6},$$

$$y=\frac{3A-2C+D}{3},$$

$$z=\frac{2C-3A+2D}{6}.$$

10. Carbonic Oxide, Marsh Gas, and Ethylic Hydride (or Methyl).

$CO=x;\ CH^4=y;\ C^2H^6=z.$

$$x=\frac{3A-2C+D}{3},$$

$$y=\frac{3A+2C-4D}{3},$$

$$z=D-A.$$

11. Hydrogen, Marsh Gas, and Acetylene.

$$H=x;\ CH^4=y;\ C^2H^2=z.$$

$$x=\frac{5A-2C-D}{2},$$

$$y=2C-3A,$$

$$z=\frac{D-2C+3A}{2}.$$

12. Hydrogen, Marsh Gas, and Ethylic Hydride (or Methyl).

$$H=x;\ CH^4=y;\ C^2H^6=z.$$

This mixture cannot be analyzed by indirect determination, since a mixture of two volumes of hydrogen with two volumes of ethylic hydride (or methyl) has the same composition as 4 volumes of marsh gas—

$$C^2H^6+H^2=2CH^4;$$

and, consequently, would give rise to the same products on combustion with oxygen as pure marsh gas—

$$C^2H^6+H^2+O^8=2CO^2+4OH^2;$$
$$2CH^4+O^8=2CO^2+4OH^2.$$

In this case it is necessary to estimate by direct determination the ethylic hydride (or methyl) in a separate portion of the gas by absorption with alcohol, another quantity of the mixture being exploded with oxygen, and the amount of carbonic anhydride produced and measured. If the quantity absorbed by alcohol$=$E, then

$$x=A-D+E,$$

$$y=D-2E,$$

$$z=E.$$

13. Hydrogen, Carbonic Oxide, Propylic Hydride.

$$H=x;\ CO=y;\ C^3H^8=z.$$

$$x=\frac{3A+4C-5D}{9},$$

$$y=\frac{3A-2C+D}{3},$$

$$z=\frac{2C-3A+2D}{9}.$$

14. Carbonic Oxide, Marsh Gas, and Propylic Hydride.

$$CO=x;\ CH^4=y;\ C^3H^8=z.$$

$$x=\frac{3A-2C+D}{3},$$

$$y=\frac{3A+4C-5D}{6},$$

$$z=\frac{D-A}{2}.$$

15. Carbonic Oxide, Ethylic Hydride (or Methyl), and Propylic Hydride.

$$CO=x;\ C^2H^6=y;\ C^3H^8=z.$$

$$x=\frac{3A-2C+D}{3},$$

$$y=\frac{3A+4C-5D}{3},$$

$$z=\frac{4D-3A-2C}{3}.$$

16. Marsh Gas, Ethylic Hydride (or Methyl), and Propylic Hydride.

$$CH^4=x;\ C^2H^6=y;\ C^3H^8=z.$$

As a mixture of two volumes of marsh gas and two of propylic hydride has the same composition as four of ethylic hydride (or methyl)—

$$CH^4+C^3H^8=2C^2H^6,$$

the volume absorbed by alcohol, and which consists of ethylic hydride (or methyl) and propylic hydride, must be determined, and another portion of the gas exploded, and the contraction measured. If E represents the volume absorbed—

$$x=A-E,$$
$$y=4A-2C+2E,$$
$$z=2C-4A-E.$$

17. Hydrogen, Carbonic Oxide, and Ethyl (or Butylic Hydride).

$$\mathrm{H}=x;\ \mathrm{CO}=y;\ \mathrm{C^4H^{10}}=z.$$

$$x=\frac{\mathrm{A}+2\mathrm{C}-2\mathrm{D}}{4},$$

$$y=\frac{3\mathrm{A}-2\mathrm{C}+\mathrm{D}}{3},$$

$$z=\frac{2\mathrm{C}+2\mathrm{D}-3\mathrm{A}}{12}.$$

18. Nitrogen, Hydrogen, Carbonic Oxide, Ethylic Hydride (or Methyl), and Butylic Hydride (or Ethyl).

$$\mathrm{N}=n;\ \mathrm{H}=w;\ \mathrm{CO}=x;\ \mathrm{C^2H^6}=y;\ \mathrm{C^4H^{10}}=z.$$

In one portion of the gas the ethylic hydride (or methyl) and the butylic hydride (or ethyl) are absorbed by alcohol; the amount absorbed = E.

A second portion of the original gas is mixed with oxygen and exploded, the amount of contraction and of carbonic anhydride being measured.

The residue now contains the nitrogen and the excess of oxygen, to this an excess of hydrogen is added, the mixture exploded, and the contraction measured. From this the quantity of nitrogen is thus obtained. Let—

G = excess of oxygen and nitrogen,
v = excess of oxygen,
n = nitrogen,
C' = contraction on explosion with hydrogen.

Then—

$$\mathrm{G}=v+n,$$

$$\mathrm{C}'=3v,$$

$$3v=\mathrm{C}'$$

$$v=\frac{\mathrm{C}'}{3},$$

$$n=\mathrm{G}-v=\mathrm{G}-\frac{\mathrm{C}'}{3}=\frac{3\mathrm{G}-\mathrm{C}'}{3}.$$

From these data the composition of the mixture can be determined—

$$w=\frac{2C-D-3E}{3},$$

$$x=\frac{3A-2C+D-3n}{3},$$

$$y=\frac{3A-2C-2D+12E-3n}{6},$$

$$z=\frac{2C-3A+2D-6E+3n}{6}.$$

MODIFICATIONS AND IMPROVEMENTS UPON THE FOREGOING PROCESSES.

§ 85. In the method of gas analysis that we have been considering, the calculations of results are somewhat lengthy, as will be seen by a reference to the example given of the analysis of a mixture of air and carbonic anhydride (p. 368). Besides this, the operations must be conducted in a room of uniform temperature, and considerable time must be allowed to elapse between the manipulation and the readings in order to allow the eudiometers to acquire the temperature of the surrounding air; and lastly, the absorption of gases by solid re-agents is slow. These disadvantages are to a great extent counterbalanced by the simplicity of the apparatus, and of the manipulation.

From time to time various chemists have proposed methods by which the operations are much hastened and facilitated, and the calculations shortened. It will be necessary to mention a few of these processes, which, however, require special forms of apparatus.

Williamson and Russell have described (Proceedings of the Royal Society, vol. ix. p. 218) an apparatus, by means of which the gases in the eudiometers are measured under a constant pressure, the correction for temperature being eliminated by varying the column of mercury in the tube so as to compensate for the alteration of volume observed in a tube containing a standard volume of moist air. In this case solid re-agents were employed in the eudiometers.

In 1864 they published (Jour. Chem. Soc., vol. xvii. 238) a further development of this method, in which the absorptions were conducted in a separate laboratory vessel, by which means the re-agents could be employed in a pasty condition and extended over a large surface.

And in 1868 Dr. Russell improved the apparatus, so that liquid re-agents could be used in the eudiometers and the analysis rapidly executed. A description of this last form of instrument is given in the Journal of the Chemical Society, vol. xxi. p. 128.

The gutta percha mercury trough employed is provided with a deep well into which the eudiometer can be depressed to any required extent, and on the surface of the mercury a wide glass cylinder, open at both ends and filled with water, is placed. The eudiometer containing the gas to be examined is suspended within the cylinder of water by means of a steel rod passing through a socket attached to a stout standard firmly fixed to the table. In a similar manner a tube containing moist air is placed by the side of the eudiometer. The clamp supporting this latter tube is provided with two horizontal plates of steel at which the column of the mercury is read off. When a volume of gas has to be measured, the pressure tube containing the moist air is raised or lowered by means of an ingeniously-contrived fine adjustment until the mercury stands very nearly at the level of one of the horizontal steel plates. The eudiometer is next raised or lowered until the column of mercury within it is at the same level, the final adjustment to bring the top of the meniscus exactly to the lower edge of the steel bar is effected by sliding a closed wide glass tube into the mercury trough. Thus we have two volumes of gas under the same pressure and temperature, and both saturated with moisture; if the temperature of the water in the cylinder increased, there would be a depression of the columns in both tubes, but by lowering the tubes, and thus increasing the pressure until the volume of air in the pressure-tube was the same as before, it would be found that the gas in the eudiometer was restored to the original volume. Again, if the barometric pressure increased, the volumes of the gases would be diminished, but, by raising the tubes to the necessary extent, the previous volumes would be obtained. Therefore in an analysis, it is only necessary to measure the gas at a pressure equal to that which is necessary to maintain the volume of moist air in the pressure-tube constant. The re-agents are introduced into the eudiometer in the liquid state by means of a small syringe made of a piece of glass tube about $\frac{1}{8}$ of an inch in diameter. For this purpose the eudiometer is raised until its open end is just below the surface of the mercury, and the syringe, which is curved upwards at the point, is depressed in the trough, passed below the edge of the water cylinder, and the extremity of the syringe introduced into the eudiometer. When a sufficient quantity of the liquid has been injected, the eudiometer is lowered and again raised so as to moisten the sides of the tube with the liquid, and thus hasten the absorption. Ten minutes was found to be a sufficient time for the absorption of carbonic anhydride when mixed with air.

To remove the liquid re-agent, a ball of moistened cotton wool is employed. The ball is made in the following manner:—A piece of steel wire is bent into a loop at one end, and some cotton wool tightly wrapped round it. It is then dipped in water and squeezed with the hand under the liquid until the air is removed. The end of the steel wire is next passed through a piece of glass tube curved near one end, and the cotton ball drawn against the curved extremity of the tube. The ball, saturated with water, is now depressed in the mercury trough, and, after as much of the water as possible has been squeezed out of it, it is passed below the eudiometer, and, by pushing the wire, the ball is brought to the surface of the mercury in the eudiometer and rapidly absorbs all the liquid re-agent, leaving the meniscus clean. The ball is removed with a slight jerk, and gas is thus prevented from adhering to it. It is found that this mode of removing the liquid can be used without fear of altering the volume of the gas in the eudiometer.

Carbonic anhydride may be absorbed by a solution of potassic hydrate, and oxygen by means of potassic hydrate and pyrogallic acid. The determination of ethylene is best effected by means of fuming sulphuric acid on a coke ball, water and dilute potassic hydrate being subsequently introduced and removed by the ball of cotton wool.

Doubtless this mode of using the liquid re-agents might be employed with advantage in the ordinary process of analysis to diminish the time necessary for the absorption of the gases. By this process of Dr. Russell's the calculations are much shortened and facilitated, the volumes read off being comparable among themselves; this will be seen by an example taken from the original memoir of the determination of oxygen in air—

		Volume in Table corresponding to reading.
Volume of air taken, . . .	130·3	132·15
Volume after absorption of oxygen by potassic hydrate and pyrogallic acid, ...	103·5	104·46

132·15
104·46
27·69 volume of oxygen in 132·15 of air.

132·15 : 27·69 : : 100 : 20·953 percentage of oxygen in air.

Dr. **Russell** has also employed his apparatus for the analysis of carbonates (Journ. Chem. Soc. N. S. vi. 310); for this purpose he adapted a graduated tube, open at both ends, to a glass flask by means of a thick piece of caoutchouc tube. Into a flask a weighed quantity of a carbonate was placed together with a vessel containing dilute acid. The position of the mercury in the graduated tube was first read off, after which the flask was shaken so as to bring the acid and carbonate in contact, and the increase in volume was due to the carbonic anhydride evolved. The results thus obtained are extremely concordant.

In eight experiments with sodic carbonate the percentage of carbonic anhydride found varied from 41·484 to 41·607, theory requiring 41·509.

Thirteen experiments with calc spar gave from 43·520 to 43·858, the theoretical percentage being 44·0; and in nine other analyses from 43·581 to 43·901 were obtained.

Two experiments were made with manganic peroxide, oxalic acid and sulphuric acid, and gave 58·156 and 58·101 per cent. of carbonic anhydride.

Some determinations of the purity of magnesium were also performed by dissolving the metal in hydrochloric acid and measuring the resulting hydrogen; four operations gave numbers varying between 8·255 and 8·282; the metal should yield 8·333.

Dr **Russell** has also employed this process for the determination of the combining proportions of nickel and cobalt (Journ. Chem. Soc. N. S., vii. 294).

MM. **Regnault** and **Reiset** described (Ann. Chim. Phys. [3] xxvi. 333) an apparatus by which absorptions could be rapidly conducted by means of liquid re-agents brought in contact with the gases in a laboratory tube. The measurements are made in a graduated tube which can be placed in communication with the laboratory tube by means of fine capillary tubes provided with stop cocks, the lower end of the measuring tube being connected by an iron socket and stopcock with another graduated tube in which the pressure, to which the gas is subjected, is measured. The measuring and pressure tubes are surrounded by a cylinder of water. An apparatus similar in principle to this has recently been constructed by Dr **Frankland**, and is fully described in the section on water analysis, § 77 page 302.

Frankland and **Ward** (Chem. Soc. Jour. vol. vi. p. 197) made several important improvements in the apparatus of **Regnault**

and Reiset. They introduced a third tube (fig. 73), closed at the top with a stopper, and which is made to act as a barometer to indicate the tension of the gas in the measuring tube, thus rendering the operation entirely independent of variations of atmospheric pressure. The correction for aqueous vapour is also eliminated by introducing a drop of water into the barometer as well as into the measuring tube the pressures produced by the aqueous vapour in the two tubes thus counterbalancing one another, so that the difference of level of the mercury gives at once the tension of the dry gas. The measuring tube is divided into ten equal divisions (which, for some purposes, require to be calibrated), and in one analysis it is convenient to make all the measurements at the same division, or to calculate the tension which would be exerted by the gas if measured at the tenth division. **Frankland** and **Ward** also adapted an iron tube, more than 760 m.m. long, at the bottom of the apparatus, which enables the operator to expand the gas to any required extent, and thus diminish the violence of the explosions which are performed in the measuring tube. During the operation a constant stream of water is kept flowing through the cylinder, which maintains a uniform temperature.

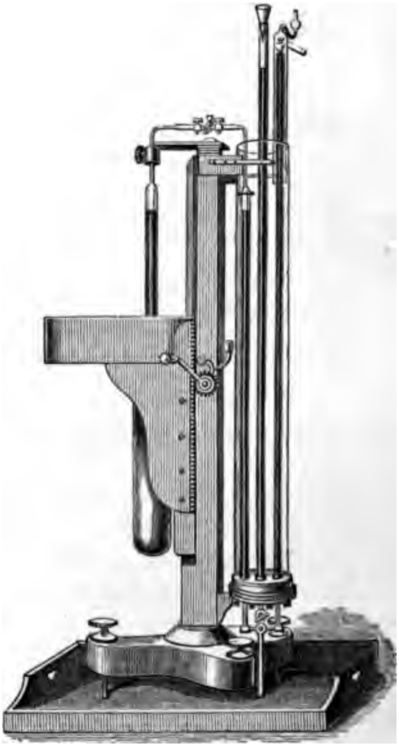

Fig. 73.

By the use of this form of apparatus the calculations of analyses are much simplified; an example of an analysis of atmospheric air will indicate the method of using the instrument:—

Volume of Air used. Determined at 5th Division on the Measuring Tube.

	m.m.
Observed height of mercury in the barometer,	673·0
Height of 5th division, ...	383·0
Tension of gas, ...	290·0
	0·5
Corrected tension of gas at 10th division, .	145·00

Volume after Admission of Hydrogen. Determined at 6th Division.

Observed height of mercury in barometer, .	772·3
Height of 6th division, ...	304·0
Tension of gas, ...	468·3
	0·6
Corrected tension at 10th division, . .	280·98

Volume after Explosion. Determined at 5th Division.

Observed height of mercury in barometer, .	763·3
Height of 5th division, ...	383·0
Tension of gas, ...	380·3
	0·5
Corrected tension at 10th division, . .	190·15
Tension of air with hydrogen, ...	280·98
Tension of gas after explosion, ...	190·15
Contraction on explosion, ...	90·83

of which one-third is oxygen.

$$\frac{90{\cdot}83}{3} = 30{\cdot}276 = \text{volumes of oxygen in } 145{\cdot}0 \text{ volumes of air}$$

$$145{\cdot}0 \;:\; 30{\cdot}276 \;::\; 100 \;:\; x$$

$$x = \frac{30{\cdot}276 \times 100}{145{\cdot}0} = 20{\cdot}88 = \text{percentage of oxygen in air.}$$

If all the measurements had been made at the same division, no correction to the 10th division would have been necessary, as the numbers would have been comparable among themselves.

Another modification of Frankland and Ward's, or Regnault's apparatus has been described by McLeod (Journ. Chem. Soc. N. S. vii. 313), in which the original pressure tube of Regnault's apparatus, or the filling tube of Frankland and Ward, is dispensed with, the mercury being admitted to the apparatus through the stopcocks at the bottom.

The measuring tube A (fig. 74) is 900 m.m. in length, and about 20 m.m. in internal diameter. It is marked with ten divisions, the first at 25 m.m. from the top, the second at 50, the third at 100, and the remaining ones at intervals of 100 m.m. In the upper part of the tube, platinum wires are sealed, and it is terminated by a capillary tube and fine glass stopcock, *a*, the capillary tube being bent at right angles at 50 m.m. above the junction. At the bottom of the tube, a wide glass stopcock *b* is sealed, which communicates, by means of a caoutchouc joint surrounded with tape and well wired to the tubes, with a branch from the barometer-tube B. This latter tube is 5 m.m. in width, and about 1200 m.m. long, and is graduated in millimetres from bottom to top. At the upper extremity a glass stopcock *d* is joined, the lower end being curved and connected by caoutchouc with a stopcock and tube C, descending through the table to a distance of 900 m.m. below the joint. It is advisable to place washers of leather at the end of the plugs of the stopcocks *c* and *b*, as the pressure of the mercury which is afterwards to be introduced has a tendency to force them out; and if this should happen, the washers prevent any great escape of mercury.

The two tubes are firmly held by a clamp D, on which rests a wide cylinder E, about 55 m.m. in diameter, surrounding the tubes, and adapted to them by a water-tight caoutchouc cork F. The cylinder is maintained in an upright position by a support at its upper end G, sliding on the same rod as the clamp. Around the upper part of the barometer-tube a syphon H is fixed by means of a perforated cork, through which the stopcock *d* passes. A small bulb-tube *e*, containing some mercury, is also fitted in this cork, so as to allow of the air being entirely removed from the syphon. The syphon descends about 100 m.m. within the cylinder, and has a branch at the top communicating by caoutchouc with a bent tube contained in a wider one J affixed to the support. A constant current of water is supplied to the cylinder through a glass tube,

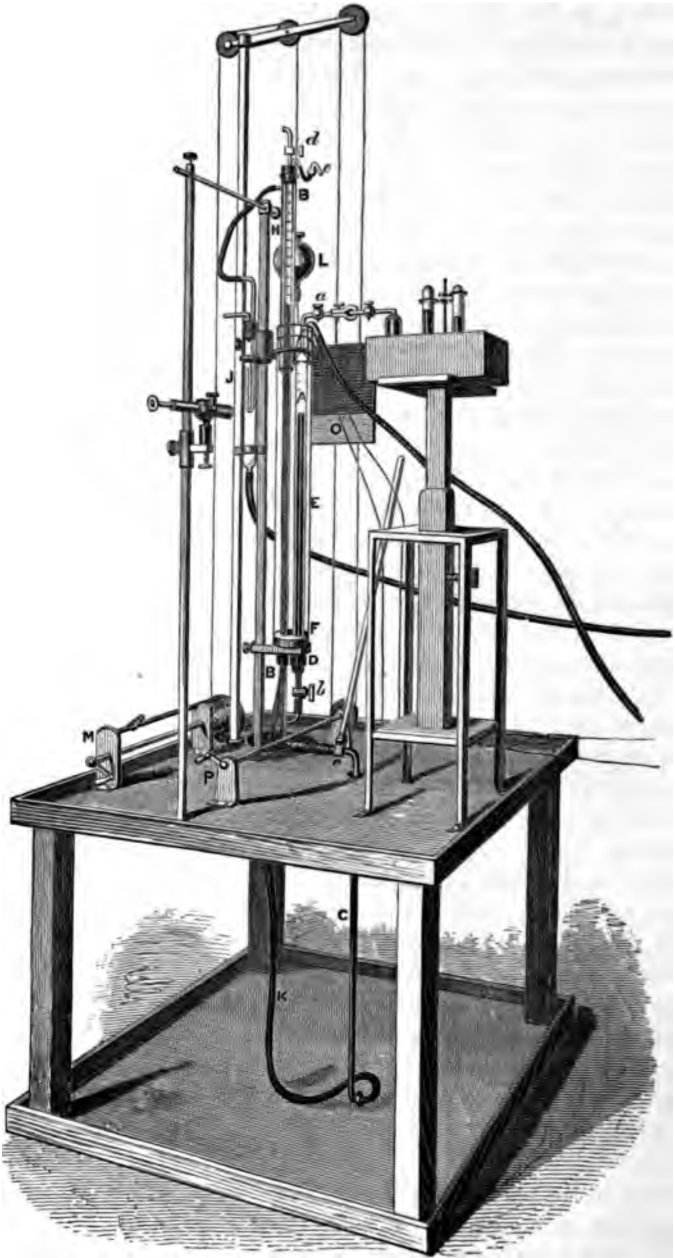

Fig. 74.

which passes to the bottom, and escapes through the syphon and tubes to the drain.

To the end of the narrow tube C, is fastened a long piece of caoutchouc tube K, covered with tape, by which a communication is established with the mercurial reservoir L, suspended by a cord, so that by means of the winch M, it may be raised above the level of the top of the barometer-tube. As the mercury frequently forces its way through the pores of the caoutchouc tube, it is advisable to surround the lower part with a piece of wide flexible tube; this prevents the scattering of the mercury, which collects in a tray placed on the floor. Into the bottom of the tray a screw must be put, to which the end of the glass tube is firmly attached by wire. The capillary stopcock *a* is provided with a steel cap, by means of which it may be adapted to a short and wide laboratory-tube capable of holding about 150 c.c., and identical in form with the one described in the section on Water Analysis (§ 77, p. 303). The mercurial trough for the laboratory-tube is provided with a stand with rings for the purpose of holding two tubes containing gases that may be required.

The apparatus is used in the same way as Frankland and Ward's, except that the mercury is raised and lowered in the tubes by the movement in the reservoir, L, instead of pouring it into the centre supply-tube.

To arrange the apparatus for use, the reservoir L is lowered to the ground, and mercury poured into it. The laboratory-tube being removed, the stopcocks are all opened, and the reservoir gradually raised. When the tube A is filled, the stopcock *a* is closed, and the reservoir elevated until mercury flows through the stopcock *d* at the top of the barometer. It is convenient to have the end of the tube above the stopcock so bent that a vessel can be placed below to receive the mercury. This bend must, of course, be so short that, when the plug of the stopcock is removed, the syphon will pass readily over. When the air is expelled from the barometer-tube, the stopcock is closed. A few drops of water must next be introduced into the barometer; this is accomplished by lowering the reservoir to a short distance below the top of the barometer, and gently opening the stopcock *d*, while a small pipette, from which water is dropping, is held against the orifice, the stopcock being closed when a sufficient amount of water has penetrated into the tube. In the same manner, a small quantity of water is passed into the measuring tube. In order to get rid of any bubbles of air which may still linger in the tubes, the reservoir is lowered to the ground so as to produce a vacuum in the apparatus; in this manner the interior surfaces of the tubes become moistened. The reservoir is now gently raised, thus refilling the tubes with mercury. Great care must be taken that the mercury does not rush suddenly against the tops of the measuring and barometer-tubes, which might cause their destruction; this may be avoided by regulating the flow of mercury by means of the stopcock *c*, which may be conveniently turned by a long key of wood, resting against the upper table of the sliding stand of the mercurial trough. When the reservoir has again been elevated above the top of the barometer, the stopcocks of the measuring and barometer tubes are opened, and the air and water which have collected allowed to escape.

The heights of the mercurial columns in the barometer corresponding to the different divisions of the measuring tube, have now to be determined. This is done by running out all the mercury from the tubes, and slowly readmitting it until the meniscus of the mercury just touches the lowest division in the measuring tube. This may be very conveniently managed by observing the division through a small telescope of short focus, and sufficiently close to the apparatus to permit of the key of the stopcock *c* being turned, while the eye is still at the telescope. When a reading is taken, the black screen O behind the apparatus must be moved by means of the winch P, until its lower edge is about a millimetre above the division. The telescope is now directed to the barometer-tube, and the position of the mercury carefully noted. As the tubes only contain aqueous vapour, and are both at the same temperature, the columns in the two tubes are those which exactly counterbalance one another, and any difference of level that may be noticed is due to capillarity.

The same operation is now repeated at each division of the tube. The measuring tube next requires calibration, an operation performed in a manner perfectly similar to that described in § 77, p. 305, namely, by filling the measuring tube with water, and weighing the quantities contained between every two divisions. The eudiometer being filled with water, and the stopcock *b* closed, the reservoir is raised and the mercury allowed to rise to the top of the barometer. The capillary stopcock *a* having been opened, the cock *b* is gently turned, and the water allowed to flow out until the mercury reaches the lowest division of the tube. A carefully-weighed flask is now supported just below the steel cap, the stopcock *b* again opened, until the next division is reached, and the quantity of water is weighed, the temperature of the water in the wide cylinder being observed. The same operation is repeated at each division, and by calculation the exact contents of the tube in cubic centimetres may be found.

In this manner a table, such as the following, is obtained:—

Division on measuring tube.	Height of Mercury in Barometer-tube corresponding to division.	Contents.	
		Cubic Centimetres.	Log.
1	756·9	8·6892	0·9389814
2	706·7	18·1621	1·2591664
3	606·8	36·9307	1·5673880
4	506·5	55·7344	1·7461232
5	406·8	74·4299	1·8717477
6	306·8	93·3306	1·9700244
7	206·9	112·4165	2·0508303
8	107·0	131·6335	2·1193666
9	7·1	151·1623	2·1794435

When a gas is to be analyzed, the laboratory-tube is filled with mercury, either by sucking the air out through the capillary stopcock, while the open end of the tube stands in the trough, or much more conveniently, by exhausting the air through a piece of flexible tube passed under the mercury to the top of the laboratory-tube, the small quantity of air remaining in the stopcock and at the top of the wide tube being very readily withdrawn. The face of one of the steel pieces is greased with a small quantity of resin cerate, and, the measuring apparatus being full of mercury, the clamp is adjusted.

Before the introduction of the gas, it is advisable to ascertain if the capillary tubes are clear, as a stoppage may arise from the admission of a small quantity of grease into one of them. For this purpose the globe L is raised above the level of the top of the measuring-tube, and the capillary stopcocks opened; if a free passage exists, the mercury will be seen to flow through the tubes. The stopcock of the laboratory-tube is now closed. When all is properly arranged, the gas is transferred into the laboratory-tube, and the stopcock opened, admitting a stream of mercury. The cock *c* is gently turned, so as just to arrest the flow of mercury through the apparatus, and the reservoir lowered to about the level of the table, which is usually sufficient. By carefully opening the cock *c*, the gas is drawn over into the measuring tube, and when the mercury has reached a point in the capillary-tube of the laboratory tube, about midway between the bend and the stopcock, the latter is quickly closed. It is necessary that this stopcock should be very perfect. This is attained by grinding the plug into the socket with fine levigated rouge and solution of sodic or potassic hydrate. By this means the plug and socket may be polished so that a very small quantity of resin cerate and a drop of oil renders it perfectly gas-tight. In grinding, care must be taken that the operation is not carried on too long, otherwise the hole in the plug may not coincide with the tubes. If this stopcock is in sufficiently good order, it is unnecessary to close the stopcock *a* during an analysis.

The mercury is allowed to flow out of the apparatus until its surface is a short distance below the division at which the measurements are to be made. The selection of the division depends on the quantity of gas and the kind of experiment to be performed with it. A saving of calculation is effected if all the measurements in one analysis are carried on at the same division. When the mercury has descended below the division, the cock *c* is closed, the reservoir raised and the black screen moved until its lower edge is about a millimetre above the division, and the telescope placed so that the image of the division coincides with the cross-wires in the eye-piece. The stopcock *c* is now gently opened until the meniscus just touches the division; the cock is closed and the height of the mercury in the barometer is measured by means of the telescope. The difference between the reading of the barometer and the number in the table corresponding to the division at which the measurement is taken, gives in millimetres the tension of the gas. The volume of the gas is found in the same table, and with the temperature, which is read off at the same time as the pressure, all the data required for the calculation of the volume of the gas at 0° and 760 m.m. are obtained. No correction is required for tension of aqueous vapour; the measuring-tube and barometer-tube being both moist, the tensions in the tubes are counterbalanced. Absorptions are performed with liquid re-agents by introducing a few drops of the liquid into the laboratory-tube, transferring the gas into it and allowing the mercury to drop slowly through the gas for about five minutes. The gas is then passed over into the measuring-tube, and the difference of tension observed corresponds to the amount of gas absorbed. It is scarcely necessary to add that the greatest care must be taken to prevent any trace of the re-agent passing the stopcock. If such an accident should occur, the measuring-tube must be washed out several times with distilled water at the conclusion of the analysis. If the re-agent is a solution of potassic hydrate it may be got rid of by introducing into the tube some distilled water, to which a drop of sulphuric acid has been added; if this liquid is found to be acid on removing it from the tube, it may be presumed that all the alkali has been neutralized.

When explosions are to be performed in the apparatus, the gas is first measured and then returned to the laboratory-tube. A quantity of oxygen or hydrogen, as the case may be, which is judged to be the proper volume, is transferred into the laboratory-tube, and some mercury is allowed to stream through the gases so as to mix them thoroughly. The mixture is next passed into the eudiometer and measured. If a sufficient quantity of the second gas has not been added, more can readily be introduced. After the measurement, it may be advisable to expand the mixture, in order to diminish the force of the explosion. This is done by allowing mercury to flow out from the tube into the reservoir. When the proper amount of expansion has been reached, the stopcocks *a* and *b* are closed. To enable the electric spark to pass between the wires, it is necessary to lower the level of the water in the cylinder. For this purpose the bent glass tube at the extremity of the syphon is made to slide easily through the cork which closes the top of the wide tube J. By depressing the bent tube, the water flows out more rapidly than before, and the level consequently falls. When the surface is below the eudiometer-wires, a spark from an induction-coil is passed, exploding the gas. The syphon tube is immediately raised, and, when the water in the cylinder has reached its original level, the gas is cool enough for measurement. 900 c.c. of mercury are amply sufficient for the whole apparatus; and as there is no cement used to fasten the wide tubes into iron sockets, a great difficulty in the original apparatus is avoided.

The following details of an analysis, in which absorptions only were performed, will show the method employed. The gas was a mixture of nitrogen, oxygen, and carbonic anhydride, and the measurements were all made at division No 1 on the eudiometer, which has been found to contain 8·6892 c.c.

Original Gas.

Temperature of water in cylinder, 15·4°.

	m.m.
Height of mercury in barometer-tube,	980·5
„ „ corresponding to Division No. 1 (see Table),	756·9
Pressure of the gas,	223·6

After absorption of the carbonic anhydride by solution of potassic hydrate—

Height of mercury in barometer tube,	941·7
„ „ corresponding to Division No. 1,	756·9
Pressure of the gas after removal of carbonic anhydride,	184·8
Pressure of original gas,	223·6
„ gas after removal of carbonic anhydride	184·8
Tension of carbonic anhydride,	38·8

After absorption of the oxygen by potassic pyrogallate—

Height of mercury in barometer-tube,	885·4
„ „ corresponding to Division No. 1,	756·9
Pressure of nitrogen,	128·5
Pressure of oxygen and nitrogen,	184·8
„ nitrogen,	128·5
„ oxygen,	56·3

These measurements, therefore, give us the following numbers:—

	m.m.
Pressure of nitrogen,	128·5
„ oxygen,	56·3
„ carbonic anhydride,	38·8
„ original gas,	223·6

If the percentage composition of the gas is required, it is readily obtained by a simple proportion, the temperature, having remained constant during the experiment:—

m.m.		m.m.				m.m.		
223·6	:	128·5	: :	100	:	57·469	per cent.	N
223·6	:	56·3	: :	100	:	25·179	„	O
223·6	:	38·8	: :	100	:	17.352	„	CO^2
						100·000		

If, however, it is necessary to calculate the number of cubic centimetres of the gases at 0° and 760 m.m., it is done by the following formulæ:—

$$\frac{8{\cdot}6892 \times 128{\cdot}5}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 1{\cdot}3906 \text{ c.c. of nitrogen.}$$

$$\frac{8{\cdot}6892 \times 56{\cdot}3}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 0{\cdot}6093 \text{ c.c. of oxygen.}$$

$$\frac{8{\cdot}6892 \times 38{\cdot}8}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 0{\cdot}4199 \text{ c.c. of carbonic anhydride}$$

$$\frac{8{\cdot}6892 \times 223{\cdot}6}{760 \times [1 + (0{\cdot}003665 \times 15{\cdot}4)]} = 2{\cdot}4198 \text{ c.c. of the original gas.}$$

If many of the calculations are to be done, they may be very much simplified by constructing a table containing the logarithms of the quotients obtained by dividing the contents of each division of the tube by $760 \times (1 + 0{\cdot}003665\ t)$. The following is a very short extract from such a table:—

T°.	Division No. 1. $\text{Log.}\ \frac{8{\cdot}6892}{760 \times (1 + \delta t)}.$	Division No. 2. $\text{Log.}\ \frac{18{\cdot}1621.}{760 \times (1 + \delta t)}.$
15·0	$\bar{2}{\cdot}03492$	$\bar{2}{\cdot}35511$
·1	$\bar{2}{\cdot}03477$	$\bar{2}{\cdot}35496$
·2	$\bar{2}{\cdot}03462$	$\bar{2}{\cdot}35481$
·3	$\bar{2}{\cdot}03447$	$\bar{2}{\cdot}35466$
·4	$\bar{2}{\cdot}03432$	$\bar{2}{\cdot}34451$

By adding the logarithms of the tensions of the gases to those in the above table, the logarithms of the quantities of gases are obtained, thus:—

Log. corresponding to Division No. 1, and 15·4°, ...	$\bar{2}{\cdot}03432$
Log. 128·5=pressure of nitrogen, .	$\bar{2}{\cdot}10890$
Log. of quantity of nitrogen, . .	0·14322=log. 1·3906
Volume of nitrogen at 0° and 760 m.m., ...	1·3906 c.c.

$\bar{2}$·03432
Log. 56·3 = pressure of oxygen, . 1·75051

Log. of quantity of oxygen, . . $\bar{1}$·78483 = log. 0·6093
Volume of oxygen at 0° and 760 m.m., ... 0·6093 c.c.

$\bar{2}$·03432
Log. 38·8 = pressure of carbonic anhydride . . . . . . 1·58883

Log. of quantity of carbonic anhydride, ... $\bar{1}$·62315 = log. 0·4199
Volume of carbonic anhydride at 0° and 760 m.m., . . . 0·4199 c.c.

$\bar{2}$·03432
Log. 223·6 = pressure of original gas, 2·34947

Log. of quantity of original gas, . 0·38379 = log. 2·4198
Volume of original gas at 0° and 760 m.m., ... 2·4198 c.c.

Nitrogen, . . .	1·3906	or	1·391 c.c.
Oxygen, . . .	0·6093	or	0·609 ,,
Carbonic anhydride, .	0·4199	or	0·420 ,,
Total, . .	2·4198	or	2·420 ,,

The following example of an analysis of coal gas will show the mode of working with this apparatus, and the various operations to be performed in order to determine the carbonic anhydride, oxygen, hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, marsh gas, carbonic oxide, and nitrogen.

The measuring tube and laboratory tube were first filled with mercury, some of the gas introduced into the laboratory tube, and passed into the apparatus.

The gas was measured at the second division.

Height of mercury in the barometer tube, .	989·0
,, ,, ,, measuring tube, .	706·8
Pressure of the gas at 16·6°, . . .	282·2

Two or three drops of a solution of potassic hydrate were now placed in the laboratory tube, and the gas passed from the measuring tube, the mercury being allowed to drop through the gas for ten minutes. On measuring again—

Height of mercury in barometer, ...	984·0

Some saturated solution of pyrogallic acid was introduced into the laboratory tube, and the gas left in contact with the liquid for ten minutes. On measuring—

Height of mercury in barometer, ...	983·6

Height of mercury when measuring original gas,	989·0
„ „ after absorption of CO^2, .	984·0
Pressure of CO^2, .	5·0
„ „ after absorption of CO^2, .	984·0
„ „ after absorption of O, .	983·6
Pressure of O, . .	0·4

The volumes of the gases being proportional to their pressures, it is simple to obtain the percentages of carbonic anhydride and oxygen in the original gas.

Original gas.		CO^2				
282·2	:	5·0	::	100	:	1·772 % CO^2
Original gas.		O				
282·2	:	0·4	::	100	:	0·142 % O
						1·914

By subtracting 1·914 from 100, we obtain the remainder, 98·086, consisting of the hydrocarbons absorbed by Nordhausen sulphuric acid, hydrogen, carbonic oxide, marsh gas, and nitrogen, thus :—

Original gas, ...	100·000
O and CO^2, ...	1·914
CnH^2n. H. CO. CH^4. N., . . .	98·086

While the gas remains in the measuring tube, the laboratory tube is removed, washed, dried, filled with mercury, and again attached to the apparatus. Much time is saved by replacing the laboratory tube by a second, which was previously ready. As a minute quantity of gas is lost in this operation, in consequence of the amount between the stop-cocks being replaced by mercury, it is advisable to pass the gas into the laboratory tube, then transfer it to the eudiometer, and measure again.

On remeasuring, the mercury in the barometer stood at 983·3
„ „ measuring tube, 706·8
Pressure of CnH^2n. H. CO. CH^4. N., 276·5

The gas is again passed into the laboratory tube, and a coke ball soaked in fuming sulphuric acid, left in contact with the gas for an hour; the bullet is then withdrawn, and some potassic hydrate introduced and left in the tube for ten minutes, in order to remove the vapours of sulphuric anhydride, and the sulphurous and carbonic anhydrides formed during the action of the Nordhausen acid on the gas. The gas is now measured again.

Height of mercury in barometer tube, . . . 969·3

„ „ „ before absorbing CnH^2n., 983·3
„ „ „ after, ... 969·3
Pressure of CnH^2n., . . . 14·0

The percentage of these hydrocarbons is thus formed :—
Gas containing CnH^2n. H. CO. CH^4. N.

$$276{\cdot}5 : \overset{CnH^2n}{14{\cdot}0} :: 98{\cdot}086 : \underline{4{\cdot}966}\ \%\ CnH^2n$$

It now remains to determine the hydrogen, carbonic oxide, marsh gas, and nitrogen in a portion of the residual gas. The laboratory tube is therefore removed, some of the gas allowed to escape, and another laboratory tube adapted to the apparatus. The portion of gas remaining is expanded to a lower ring (in this special case to the third division), and the tension measured :—

Height of mercury in the barometer tube, . 642·2
„ „ measuring tube, . 606·7
Pressure of residue, . . 35·5

An excess of oxygen has now to be added. For this purpose the gas is passed into the laboratory tube, and about five times its volume of oxygen introduced from a test tube or gas pipette. The necessary quantity of oxygen is conveniently estimated by the aid of rough graduations on the laboratory tube, which are made by introducing successive quantities of air from a small tube in the manner previously described for the calibration of eudiometers.

After the introduction of the oxygen, the mixed gases are passed into the eudiometer and measured.

Height of mercury in the eudiometer after addition of O, 789·5

The mixture has now to be exploded, and when the pressure is considerable, it is advisable to expand the gas so as to moderate the violence of the explosion. When sufficiently dilated, the stopcock at the bottom of the eudiometer is closed, the level of the water lowered beneath the platinum wires by depressing the syphon, and the spark passed. The explosion should be so powerful that it should be audible, and the flash visible in not too bright daylight.

The stopcock at the bottom of the eudiometer is now opened, and the gas measured.

Height of mercury in barometer after explosion,	732·5

The difference between this reading and the previous one gives the contraction produced by the explosion :—

Height of mercury in barometer before explosion,	789·5
" " " after "	732·5
Contraction = C., .	57·0

It is now necessary to estimate the amount of carbonic anhydride formed. This is done by absorbing with potassic hydrate as before described.

Height of mercury in barometer tube after absorbing CO^2,	715·8

This number deducted from the last reading gives the carbonic anhydride.

Height of mercury in barometer after exploding, .	732·5
" " " absorbing CO^2, .	715·8
Carbonic anhydride = D, .	16·7

It now remains to determine the quantity of oxygen which was not employed in the explosion, and which excess now exists mingled with the nitrogen. For this purpose a volume of hydrogen about three times as great as that of the residual gas is added, in the same way as the oxygen was previously introduced, and the pressure of the mixture determined.

Height of mercury in barometer after adding H, .	1031·3

This mixture is exploded and another reading taken.

Height of mercury in barometer after exploding with H,	706·7

This number subtracted from the former, and the difference divided by 3, gives the excess of oxygen.

Height of mercury in barometer before exploding with H, ...	1031·3
Height of mercury in barometer after exploding with H,	706·7
	3)324·6
Excess of oxygen, .	108·2

In order to obtain the quantity of nitrogen in the gas analyzed, this number has to be deducted from the volume of gas remaining after the explosion with oxygen and the removal of the carbonic anhydride.

Height of mercury in barometer after absorbing CO^2,	715·8
„ eudiometer at division No. 3, .	606·7
„ Nitrogen and excess of oxygen, .	109·1
„ Excess of oxygen, . .	108·2
„ Nitrogen, . . .	0·9

We have now all the data necessary for the calculation of the composition of the coal gas. It is first requisite to calculate the proportion of the combustible gas present in the coal gas, which is done by deducting the sum of the percentages of gas determined by absorption from 100.

Percentage of carbonic anhydride, . .	1·772
„ oxygen, . . .	0·142
„ CnH^2n, . . .	4·966
CO^2. O. CnH^2n, ...	6·880
Original gas, ...	100·000
CO^2. O. CnH^2n, ...	6·880
H. CO. CH^4. N, ...	93·120

The formulæ for the calculation of the analysis of a mixture of hydrogen, carbonic oxide, and marsh gas, are (see p. 383).

$$\text{Hydrogen} = x = A - D$$

$$\text{Carbonic oxide} = y = \frac{3A - 2C + D}{3}$$

$$\text{Marsh gas} = z = \frac{2C - 3A + 2D}{3}$$

$$A = 35{\cdot}5 - 0{\cdot}9 = 34{\cdot}6$$
$$C = 57{\cdot}0$$
$$D = 16{\cdot}7$$

$$\begin{aligned} A &= 34{\cdot}6 \\ D &= \underline{16{\cdot}7} \\ & \ 17{\cdot}9 = x = \text{hydrogen in } 35{\cdot}5 \text{ of the gas exploded with oxygen.} \end{aligned}$$

$$\begin{aligned} A &= 34{\cdot}6 & \qquad C &= 57{\cdot}0 \\ & \ \underline{3} & & \ \underline{2} \\ 3A &= 103{\cdot}8 & 2C &= \underline{114{\cdot}0} \\ D &= \underline{16{\cdot}7} \\ 3A + D &= 120{\cdot}5 \\ 2C &= \underline{114{\cdot}0} \\ 3)\ & \ \underline{6{\cdot}5} = 3A + D - 2C \end{aligned}$$

$$\frac{3A+D-2C}{3} = \underline{2{\cdot}167} = y = \text{carbonic oxide in } 35{\cdot}5 \text{ of the gas.}$$

$$\begin{aligned} D &= 16{\cdot}7 \\ & \ \underline{\phantom{16{\cdot}}2} \\ 2D &= 33{\cdot}4 \\ 2C &= \underline{114{\cdot}0} \\ 2D + 2C &= 147{\cdot}4 \\ 3A &= \underline{103{\cdot}8} \\ 3)\ & \ \underline{43{\cdot}6} \qquad = 2D + 2C - 3A \end{aligned}$$

$$\frac{2D+2C-3A}{3} = \underline{14{\cdot}533} = z = \text{marsh gas in } 35{\cdot}5 \text{ of the gas.}$$

These numbers are readily transformed into percentages, thus :—

35·5 : 17·9 : : 93·12 : 46·952% of hydrogen.
35·5 : 2·167 : : 93·12 : 5·684% of carbonic oxide.
35·5 : 14·533 : : 93·12 : 38·122% of marsh gas.
35·5 : 0·9 : : 93·12 : 2·361% of nitrogen.

This completes the calculations, the results of which are as follows :—

Hydrogen . . .	46·952
Marsh gas . . .	38·122
C_nH_{2n} . . .	4·966
Carbonic oxide . .	5·684
Carbonic anhydride . .	1·772
Oxygen . . .	0·142
Nitrogen . . .	2·361
	99·999

It is obvious that this analysis is not quite complete, since it does not give any notion of the composition of the hydrocarbons absorbed by the Nordhausen acid. To determine this, some of the original gas, after the removal of carbonic anhydride and oxygen, is exploded with oxygen, and the contraction and carbonic anhydride produced are measured. The foregoing experiments have shown the effect due to the hydrogen, carbonic oxide, and marsh gas, the excess obtained in the last explosion being obviously caused by the hydrocarbons dissolved by the sulphuric acid, and from these data the composition of the gas may be calculated.

It may be remarked that analyses of this kind were performed with the apparatus at the rate of two a day when working for seven hours

It may be useful to show how this analysis appears in the laboratory note-book:—

Analysis of Coal Gas.

989·0 706·8 282·2	(16·6°) original gas	989·0 984·0 5·0 = CO^2	984·0 983·6 0·4 = O
984·0	Aft. absorb. CO^2	282·2 : 5·0 : : 100 : 1·772 CO^2 282·2 : 0·4 : : 100 : 0·142 O	
983·6	Aft. absorb. O		1·914
983·3	Remeasured	100·000 1·914 CO^2.O 98·086 C^nH^{2n}. H. CO. CH^4. N	
969·3	Aft. absorb. C^nH^{2n}	983·3 706·8 276·5	983·3 969·3 14·0 C^nH^{2n}
642·2 606·7 35·5	Portion of Residue		276·5 : 14·0 : : 98·086 : 4·966 C^nH^{2n}
789·5	with O	35·5 = H. CO. CH^4. N 0·9 = N 34·6 = H. CO. CH^4 = A	CO^2 = 1·772 O = 0·142 C^nH^{2n} = 4·966 6·880
732·5	Aft. expl.		
715·8	Aft. absorb. CO^2	789·5 732·5 57·0 = contraction = C	732·5 715·8 16·7 = CO^2 = D
1031·3	with H		
706·7	Aft. expl.	1031·3 706·7 3) 324·6 108·2 = O	715·8 606·7 109·1 = N + O 108·2 = O 0·9 = N

$$\begin{array}{lr}
H = x = A - D & = 17\cdot9 \\
CO = y = \dfrac{3A - 2C + D}{3} & = 2\cdot167 \\
CH^4 = z = \dfrac{2C - 3A + 2D}{3} & = 14\cdot533 \\
\cline{2-2}
 & 34\cdot600 \\
\cline{2-2}
\end{array}$$

$$\begin{array}{rl}
34\cdot6 & = A \\
16\cdot7 & = D \\
\hline
17\cdot9 & = x = H \\
\hline
 & \\
57\cdot0 & = C \\
2 & \\
\hline
114\cdot0 & = 2C \\
\hline
\end{array}
\qquad
\begin{array}{rrl}
 & 34\cdot6 & = A \\
 & 3 & \\
\cline{2-2}
 & 103\cdot8 & = 3A \\
 & 16\cdot7 & = D \\
\cline{2-2}
 & 120\cdot5 & = 3A + D \\
 & 114\cdot0 & = 2C \\
\cline{2-2}
3) & 6\cdot5 & = 3A + D - 2C \\
\cline{2-2}
 & 2\cdot167 & = y = CO \\
\cline{2-2}
\end{array}
\qquad
\begin{array}{rrl}
 & 16\cdot7 & = D \\
 & 2 & \\
\cline{2-2}
 & 33\cdot4 & = 2D \\
 & 114\cdot0 & = 2C \\
\cline{2-2}
 & 147\cdot4 & = 2C + 2D \\
 & 103\cdot8 & = 3A \\
\cline{2-2}
3) & 43\cdot6 & = 2D + 2C - 3A \\
\cline{2-2}
 & 14\cdot533 & = z = CH^4 \\
\cline{2-2}
\end{array}$$

$$\begin{array}{rl}
100\cdot000 & \\
6\cdot880 & CO.\ O.\ CnH^2n \\
\hline
93\cdot120 & H.\ CO.\ CH^4.\ N \\
\hline
\end{array}
\qquad
\begin{array}{l}
35\cdot5 : 17\cdot9 :: 93\cdot12 : 46\cdot952\ H \\
35\cdot5 : 2\cdot167 :: 93\cdot12 : 5\cdot684\ CO \\
35\cdot5 : 14\cdot533 :: 93\cdot12 : 38\cdot122\ CH^4 \\
35\cdot5 : 0\cdot9 :: 93\cdot12 : 2\cdot361\ N
\end{array}$$

$$\begin{array}{lcr}
H & = & 46\cdot952 \\
CH^4 & = & 38\cdot122 \\
CnH^2n & = & 4\cdot966 \\
CO & = & 5\cdot684 \\
CO^2 & = & 1\cdot772 \\
O & = & 0\cdot142 \\
N & = & 2\cdot361 \\
\cline{3-3}
 & & 99\cdot999 \\
\cline{3-3}
\end{array}$$

APPENDIX.

ZINC. § 45.3.

Schaffner's modification of this process, and which is used constantly at the laboratory of the Vieille Montagne Zinc Works, is conducted as follows:—For ores containing over 35% zinc, 0·5 gm. is taken; for poorer ones, 1 gm. to 2 gm. Silicates, carbonates, or oxides, are treated with hydrochloric acid, adding a small proportion of nitric acid at boiling heat to peroxidize the iron. Sulphur ores are treated with *aqua regia*, evaporated to dryness, and the zinc afterwards extracted by hydrochloric acid; the ammoniacal solution is then prepared as described in § 45.2, page 147.

The Analytical process: The titration is carried out with a normal solution of sodic sulphide; the Vieille Montagne laboratory uses ferric chloride as an indicator according to Schaffner's method. For this purpose a single drop or some few drops of this chloride are let fall into the ammoniacal solution of zinc. The perchloride which has been added is at once converted into red flakes of hydrated ferric oxide, which float at the bottom of the flask. If sodic sulphide be dropped from a Mohr's burette into these solutions of zinc, a white precipitate of zinc sulphide is at once thrown down, and the change in the colour of the flakes of iron from red to black shows the moment when all the zinc is sulphuretted, and the titration is ended. It is advisable to keep the solution for titration at from 40 to 60°C. Titration carried out under exactly equal conditions, with a known and carefully-weighed proportion of zinc, gives comparative data for calculation, and thus for the determination of the contents of any zinc solution by means of a simple equation. If, for example, 30·45 c.c. of sodic sulphide have been used to precipitate 0·25 grammes of zinc (subtracting the necessary correction) the solution of the sodic sulphide has a composition such that 1 c.c. of it will precipitate 8·21 milligrammes of zinc ($30{\cdot}45 : 0{\cdot}25 = 1 : x$, and therefore $x = 0{\cdot}00821$).

Practice has pointed out the following concentrations and proportions as best suited for the successful execution of these titrations.

The sodic sulphide solution which is used for titration must be such, that 1 c.c. precipitates 8 to 9 milligrammes of zinc. The solution which contains the zinc which has to be estimated will comply with the required conditions if its volume varies between the limits of 175 and 225 c.c. only. It is advisable that all solutions of zinc should be pretty equally saturated with ammonia, so that the ferric chloride added as an indicator may be precipitated in the same manner in all samples, and so that the flakes of iron may be always clean and clear.

When the method employed by Schaffner was first brought into use, it was soon found that the entire number of cubic centimetres of sodic sulphide used in an assay should not be considered as exclusively devoted to the sulphuretting of the zinc, since a certain part goes to cause the blackening, *i.e.*, the sulphuretting of the iron. The amount of the titrating reagent required for sulphuretting the iron can be determined by an experiment with a few drops of ferric chloride, added to a simple solution of ammonia which contains no other substance. Since the sulphurization of these flakes of iron is merely superficial, the amount of reagent used is altogether unimportant. Close investigation has shown that the amount of sodic sulphide used does not, perhaps, stand in any proportion to the number of drops of perchloride of iron, but in direct ratio with the total volume of the fluid used in the estimation.

The value which has to be subtracted from the quantities of the titrating fluid used, is, therefore, proportionate to the volume of the titrated solutions of zinc, and the amount of the correction is, with the operation as above detailed, equal to 0·7 c.c. of sodic sulphide to 100 c.c. by volume of the fluids subjected to titration. Suppose, for example, that a dissolved quantity of zinc, Z, makes a solution of 100 c.c., and an equal quantity of zinc, Z^1, has when dissolved a volume of 200 c.c : for Z, 32·4 c.c. sodic sulphide will be used, while for Z^1, 33·1 c.c. are required. The difference of 0·7 c.c. must necessarily, therefore, be ascribed to the difference of 100 c.c. which exists between the bulks of the two solutions. In practice the volume of the fluid titrated is measured at the end of the titration, and from the sum of the cubic centimetres used, there is subtracted the figure which corresponds to that of the volume measured.

Example: The sodic sulphide used in an assay is 36·8 c.c., the volume of the titrated solution 185 c.c. The value of the correction required is got by the following proportions: $100 : 185 = 0{\cdot}7 : x$, therefore $x = 1{\cdot}29$ c.c., there consequently remains $36{\cdot}80 - 1{\cdot}29 = 35{\cdot}51$ c.c. sodic sulphide, which was used for precipitating the zinc contained in the solution.

The essential point of the volumetric process practised at the Vieille Montagne is the perfect uniformity of working adopted in the assays with reference to the volume of the solutions and reagents used. In titrating, the same quantities of ferric oxide in flakes, hydrochloric acid and ammonia, are steadily used. Work is done always at one temperature and in the same time, particularly at the end of the operation, when the iron begins to take on that characteristic colour which the flakes take at the edges—points which should not be overlooked. As a further precaution, the titrating apparatus is provided in duplicate, the assay, for safety's sake, being always made in duplicate. It is immovable, and permits the execution of several titrations without the necessity of a too frequent renewal of sodic sulphide. It consists of a yellow flask of large capacity which supplies two Mohr's burettes under which the beakers can be placed and warmed. A mirror shows by reflection the iron flakes which settle down after shaking the liquid.

BISMUTH. § 50.

M. Pattison Muir, has announced a method for the volumetric estimation of this metal which appears to give exceedingly good results (Journ. Chem. Soc., 1866, p. 483).

The method is based upon the reaction which occurs between a slightly acid solution of bismuthic nitrate, and potassic chromate, or bichromate; the latter salt appears to be best adapted to the purpose. The precipitate of bismuthic chromate possesses a composition which is not accurately known, but it suffices to say, that with a slight excess of bichromate the whole of the bismuth is precipitated; and the presence of an excess of bichromate is known by bringing a drop of the supernatant liquid in contact with a drop of silver nitrate on a white plate, so as to obtain the characteristic colour of silver chromate.

The standard solution of bichromate is best fixed upon a solution of bismuth of known strength.

The Analytical process: A convenient quantity of bismuth in nitric acid solution, say, from 0·3 to 0·5 gm. in 100 c.c. of liquid is taken, and sufficient ammonia added to remove the chief excess of acid; the fluid is then boiled and ammonia carefully added until only faintly acid. A faint precipitate will form, but this does not interfere with the accuracy of the result; the bichromate solution is then added from the burette with boiling after each addition; the precipitate allowed to settle, and so continued until a drop brought in contact with the silver nitrate gives rise to the red silver chromate; the precipitate does not appear immediately, hence a few moments must be allowed after each testing.

A convenient strength of bichromate solution is about 10 gm. per litre.

The numbers obtained by Pattison Muir, with known weights of bismuth are very satisfactory; the method, however, is not available in the presence of chlorides nor other metals, the bismuth must therefore be separated from such combinations previous to estimation. Löwe and Pearson have previously advocated the estimation of bismuth as chromate, the former, gravimetrically, and the latter, volumetrically; but the process here given is undoubtedly the best.

NITRITES.

Very dilute solutions of nitrous acid in combination with alkaline or earthy bases such as naturally occur in drinking waters can be titrated with very fair results according to Fresenius, as follows:

250 c.c. of the water is acidified with acetic acid, placed in a retort and about 100 c.c. distilled into a 250 c.c. flask, the measure being afterwards made up with pure distilled water; this fluid is then acidified with pure sulphuric acid and titrated with a very weak solution of potassic permanganate.

Nitrous acid may be thus separated without any danger of oxidation; the presence of nitrates or other ordinary constituents of water do not in the slightest interfere with the accuracy of results; the greater part of the acid distils over in the first 20 or 30 c.c.

It is necessary that the solution should be very dilute, not exceeding about 6 milligrammes per litre of nitrous acid; if much stronger than this irregularities occur which interfere with accuracy.

The best qualitative test for nitrites is, to acidify the water moderately with pure sulphuric acid, then adding potassic iodide and starch liquor, the occurrence of the dark blue colour of starch iodide reveals the presence of nitrites immediately, this test may be conveniently applied before distilling any sample of water so as to form a judgment of the amount of nitrites present.

Example: Some solution of potassic nitrite was added to pure water, and on testing in the above manner a deep blue solution was obtained.

250 c.c. of the same liquid were then acidified with sulphuric acid and titrated with a permanganate solution of which 35 c.c.

represented 0·02 gm. iron or 0·0068 gm. nitrous acid—the quantity required was 8·2 c.c. 250 c.c. were then acidified with acetic acid, and about half of the liquid distilled and diluted to 250 c.c., then acidified with sulphuric acid and titrated with the permanganate; the quantity required was 7·5 c.c.

The first experiment showed the presence of 0·00159 gm. of nitrous acid and the second 0·00146 gm., or a loss in the 250 c.c. of 0·00013 gm.

URANIUM. § 53.

The estimation of this metal in the form of nitrate, chloride, acetate, or oxide, can of course be made by simply reversing the process for phosphoric acid as described in § 69.

Recovery of Uranium Residues.

Uranic phosphate, or ammonio-phosphate, as they occur in the estimation of phosphoric acid volumetrically or by weight, should be collected in a suitable vessel until a sufficient amount to recover has accumulated. A little excess of sodic or calcic phosphate should always be present to insure the precipitation of all the uranium.

The recovery is best done as follows:—

Wash the precipitate two or three times with warm water by decantation so as to remove the bulk of soluble salts, then pour the moist precipitate into a warm saturated solution of ammonic carbonate until no more is dissolved; or rather, let there be sufficient ammonic carbonate solution to dissolve the whole of the precipitate; any iron present will be left undissolved. The solution is then filtered clear, and the phosphoric acid precipitated with 'magnesia mixture' (see page 225); after standing 8 or 10 hours the solution of uranium in ammonic carbonate is filtered off, and evaporated to about half its bulk, when a basic salt of uranium and ammonic carbonate will begin to separate; hydrochloric acid is then added in excess and the mixture boiled to drive off all traces of carbonic acid. Liquid ammonia free from carbonate is then added in excess, which at once precipitates pure ammonio-uranic oxide in such a form as to be readily washed in a filter, after which it may be dissolved in acetic or nitric acid ready for standard solution; the loss is under 5 per cent.

E for Correction of Volumes of Gases for Temperature, according to the Formula V, $= \frac{V \times B}{760 \times (1+\delta t)}$

1 + δ t from 0° to 30°. δ = 0·003665.

+ δ t	Log. (1 + δ t)	t	1 + δ t	Log. (1 + δ t)	t	1 + δ t	Log. (1 + δ t)
000000	0·000 0000	5°·0	1·0183250	0·007 8864	10°·0	1·0366500	0·015 6321
003665	1591	·1	1·0186915	0·008 0427	·1	1·0370165	7857
007330	3182	·2	1·0190580	1989	·2	1·0373830	9392
010995	4772	·3	1·0194245	4551	·3	1·0377495	0·016 0926
014660	6362	·4	1·0197910	5112	·4	1·0381160	2459
018325	7951	5·5	1·0201575	6672	10·5	1·0384825	3992
021990	9519	·6	1·0205240	8232	·6	1·0388490	5524
025655	0·001 1127	·7	1·0208905	9791	·7	1·0392155	7056
029320	2714	·8	1·0212570	0·009 1350	·8	1·0395820	8587
032985	4301	5 9	1·0216235	2908	10·9	1·0399485	0·017 0118
036650	0·001 5888	6·0	1·0219900	0·009 4466	11·0	1·0403150	0·017 1648
040315	7474	·1	1·0223565	6023	·1	1·0406815	3178
043980	9059	·2	1·0227230	7580	·2	1·0410480	4707
047645	0·002 0643	·3	1·0230895	9136	·3	1·0414145	6236
051310	2227	·4	1·0234560	0·010 0692	·4	1·0417810	7764
054975	3810	6·5	1·0238225	2247	11·5	1·0421475	9292
058640	5393	·6	1·0241890	3802	·6	1·0425140	0·018 0819
062305	6974	·7	1·0245555	5356	·7	1·0428805	2346
065970	8556	·8	1·0249220	6909	·8	1·0432470	3872
069635	0·003 0137	6·9	1·0252885	8461	11·9	1·0436135	5397
073300	0·003 1718	7·0	1·0256550	0·011 0013	12·0	1·0439800	0·018 6922
076965	3298	·1	1·0260215	1565	·1	1·0443465	8446
080630	4877	·2	1·0263880	3116	·2	1·0447130	9970
084295	6455	·3	1·0267545	4666	·3	1·0450795	0·019 1493
087960	8033	·4	1·0271210	6216	·4	1·0454460	3016
091625	9611	7·5	1·0274875	7765	12·5	1·0458125	4538
095290	0·004 1188	·6	1·0278540	9314	·6	1·0461790	6060
098955	2765	·7	1·0282205	0·012 0862	·7	1·0465455	7581
102620	4341	·8	1·0285870	2410	·8	1·0469120	9102
106285	5916	7·9	1·0289535	3957	12·9	1·0472785	0·020 0622
109950	0·004 7490	8·0	1·0293200	0·012 5504	13·0	1·0476450	0·020 2141
113615	9063	·1	1·0296865	7050	·1	1·0480115	3660
117280	0·005 0636	·2	1·0300530	8596	·2	1·0483780	5179
120945	2210	·3	1·0304195	0·013 0141	·3	1·0487445	6697
124610	3782	·4	1·0307860	1685	·4	1·0491110	8214
128275	5354	8·5	1·0311525	3229	13·5	1·0494775	9731
131940	6926	·6	1·0315190	4772	·6	1·0498440	0·021 1248
135605	8497	·7	1·0318855	6315	·7	1·0502105	2764
139270	0·006 0067	·8	1·0322520	7857	·8	1·0505770	4279
142935	1636	8·9	1·0326185	9399	13·9	1·0509435	5794
146600	0·006 3205	9·0	1·0329850	0·014 0940	14·0	1·0513100	0·021 7308
150265	4773	·1	1·0333515	2481	·1	1·0516765	8821
153930	6341	·2	1·0337180	4021	·2	1·0520430	0·022 0334
157595	7909	·3	1·0340845	5561	·3	1·0524095	1847
161260	9476	·4	1·0344510	7100	·4	1·0527760	3359
164925	0·007 1042	9·5	1·0348175	8638	14.5	1·0531425	4871
168590	2607	·6	1·0351840	0·015 0175	·6	1·0535090	6382
172255	4172	·7	1·0355505	1712	·7	1·0538755	7893
175920	5736	·8	1·0359170	3249	·8	1·0542420	9403
179585	7300	9·9	1·0362835	4785	14·9	1·0546085	0·023 0193

TABLE for Correction of Volumes of Gases—*continued.*

t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$	t	$1 + \delta t$	Log. $(1 + \delta t)$
15°·0	1·0549750	0·023 2422	20°·0	1·0730000	0·030 7211	25°·0	1·0916250	0·038 0734
·1	1·0553415	3930	·1	1·0736665	8694	·1	1·0919915	2192
·2	1·0557080	5438	·2	1·0740330	0·031 0176	·2	1·0923580	3649
·3	1·0560745	6945	·3	1·0743995	1658	·3	1·0927245	5106
·4	1·0564410	8452	·4	1·0747660	3139	·4	1·0930910	6563
15·5	1·0568075	9959	20·5	1·0751325	4620	25·5	1·0934575	8019
·6	1·0571740	0·024 1465	·6	1·0754990	6100	·6	1·0938240	9474
·7	1·0575405	2970	·7	1·0758655	7580	·7	1·0941905	0·039 0929
·8	1·0579070	4475	·8	1·0762320	9058	·8	1·0945570	2384
15·9	1·0582735	5979	20·9	1·0765985	0·032 0538	·9	1·0949235	3838
16·0	1·0586400	0·024 7483	21·0	1·0769650	0·032 2016	26·0	1·0952900	0·039 5291
·1	1·0590065	8986	·1	1·0773315	3493	·1	1·0956565	6744
·2	1·0593730	0·025 0489	·2	1·0776980	4971	·2	1·0960230	8197
·3	1·0597395	1991	·3	1·0780645	6447	·3	1·0963895	9649
·4	1·0601060	3492	·4	1·0784310	7924	·4	1·0967560	0·040 1101
16·5	1·0604725	4993	21·5	1·0787975	9399	26·5	1·0971225	2552
·6	1·0608390	6494	·6	1·0791640	0·033 0874	·6	1·0974890	4003
·7	1·0612055	7994	·7	1·0795305	2349	·7	1·0978555	5453
·8	1·0615720	9494	·8	1·0798970	3824	·8	1·0982220	6902
16·9	1·0619385	0·026 0993	21·9	1·0802635	5298	·9	1·0985885	8351
17·0	1·0623050	0·026 2492	22·0	1·0806300	0·033 6771	27·0	1·0989550	0·040 9800
·1	1·0626715	3990	·1	1·0809965	8244	·1	1·0993215	0·041 1248
·2	1·0630380	5488	·2	1·0813630	9716	·2	1·0996880	2696
·3	1·0634045	6985	·3	1·0817295	0·034 1187	·3	1·1000545	4143
·4	1·0637710	8482	·4	1·0820960	2658	·4	1·1004210	5589
17·5	1·0641375	9978	22·5	1·0824625	4129	27·5	1·1007875	7035
·6	1·0645040	0·027 1474	·6	1·0828290	5599	·6	1·1011540	8481
·7	1·0648705	2968	·7	1·0831955	7069	·7	1·1015205	9926
·8	1·0652370	4462	·8	1·0835620	8538	·8	1·1018870	0·042 1371
17·9	1·0656035	5956	22·9	1·0839285	0·035 0007	·9	1·1022535	2815
18·0	1·0659700	0·027 7450	23·0	1·0842950	0·035 1475	28·0	1·1026200	0·042 4259
·1	1·0663365	8943	·1	1·0846615	2943	·1	1·1029865	5702
·2	1·0667030	0·028 0435	·2	1·0850280	4410	·2	1·1033530	7145
·3	1·0670695	1927	·3	1·0853945	5877	·3	1·1037195	8587
·4	1·0674360	3418	·4	1·0857610	7343	·4	1·1040860	0·043 0029
18·5	1·0678025	4909	23·5	1·0861275	8809	28·5	1·1044525	1470
·6	1·0681690	6399	·6	1·0864940	0·036 0274	·6	1·1048190	2911
·7	1·0685355	7889	·7	1·0868605	1739	·7	1·1051855	4352
·8	1·0689020	9379	·8	1·0872270	3203	·8	1·1055520	5792
18·9	1·0692685	0·029 0868	23·9	1·0875935	4666	·9	1·1059185	7232
19·0	1·0696350	0·029 2356	24·0	1·0879600	0·036 6129	29·0	1·1062850	0·043 8671
·1	1·0700015	3844	·1	1·0883265	7592	·1	1·1066515	0·044 0110
·2	1·0703680	5331	·2	1·0886930	9054	·2	1·1070180	1548
·3	1·0707345	6818	·3	1·0890595	0·037 0516	·3	1·1073845	2986
·4	1·0711010	8304	·4	1·0894260	1978	·4	1·1077510	4423
19·5	1·0714675	9790	24·5	1·0897925	3439	29·5	1·1081175	5859
·6	1·0718340	0·030 1275	·6	1·0901590	4899	·6	1·1084840	7295
·7	1·0722005	2760	·7	1·0905255	6359	·7	1·1088505	8730
·8	1·0725670	4244	·8	1·0908920	7818	·8	1·1092170	0·045 0165
19·9	1·0729335	5728	·9	1·0912585	9276	·9	1·1095835	1600
						30·0	1·1099500	0·045 3035

E for Correction of Volumes of Gases for Temperature,
iving the Divisor for the Formula $V^1 = \frac{V \times B}{760 \times (1+\delta t)}$

× δt).	Log. [760 × (1 + δt)].	t	760 × (1 + δt).	Log. [760 × (1 + δt)].	t	760 × (1 + δt).	Log. [760 × (1 + δt)].
0000	2·880 8136	4·0	771·1416	2·887 1341	8·0	782·2832	2·893 3640
2785	9727	·1	771·4201	2909	·1	782·5617	5186
5571	2·881 1318	·2	771·6987	4477	·2	782·8403	6732
8356	2908	·3	771·9772	6045	·3	783·1188	8277
1142	4498	·4	772·2558	7612	·4	783·3974	9821
3927	6087	4·5	772·5343	9178	8·5	783·6759	2·894 1365
6712	7675	·6	772·8128	2·888 0743	·6	783·9544	2908
9498	9263	·7	773·0914	2308	·7	784·2330	4451
2283	2·882 0850	·8	773·3699	3872	·8	784·5115	5993
5069	2437	·9	773·6485	5436	·9	784·7901	7535
7854	2·882 4024	5·0	773·9270	2·888 7000	9·0	785·0686	2·894 9076
0639	5610	·1	774·2055	8563	·1	785·3471	2·895 0617
3425	7195	·2	774·4841	2·889 0125	·2	785·6257	2157
6210	8779	·3	774·7626	1687	·3	785·9042	3697
8996	2·883 0363	·4	775·0412	3248	·4	786·1828	5236
1781	1946	5·5	775·3197	4808	9·5	786·4613	6774
4566	3528	·6	775·5982	6368	·6	786·7398	8311
7352	5111	·7	775·8768	7927	·7	787·0184	9848
0137	6692	·8	776·1553	9486	·8	787·2969	2·896 1385
2923	8273	·9	776·4339	2·890 1044	·9	787·5755	2921
5708	2·883 9854	6·0	776·7124	2·890 2602	10·0	787·8540	2·896 4457
8493	2·884 1434	·1	776·9909	4159	·1	788·1325	5993
1279	3013	·2	777·2695	5716	·2	788·4111	7528
4064	4591	·3	777·5480	7272	·3	788·6896	9062
6850	6169	·4	777·8266	8828	·4	788·9682	2·897 0595
9635	7747	6·5	778·1051	2·891 0383	10·5	789·2467	2128
2420	9324	·6	778·3836	1938	·6	789·5252	3660
5206	2·885 0901	·7	778·6622	3492	·7	789·8038	5192
7991	2477	·8	778·9407	5045	·8	790·0823	6723
0777	4052	·9	779·2193	6597	·9	790·3609	8254
3562	2·885 5626	7·0	779·4978	2·891 8149	11·0	790·6394	2·897 9784
6347	7199	·1	779·7763	9701	·1	790·9179	2·898 1314
9133	8772	·2	780·0549	2·892 1252	·2	791·1965	2843
1918	2·886 0345	·3	780·3334	2802	·3	791·4750	4372
4704	1918	·4	780·6120	4352	·4	791·7536	5900
7489	3490	7·5	780·8905	5901	11·5	792·0321	7428
0274	5062	·6	781·1690	7450	·6	792·3106	8955
3060	6633	·7	781·4476	8998	·7	792·5892	2·899 0482
5845	8203	·8	781·7261	2·893 0546	·8	792·8677	2008
8631	9772	·9	782·0047	2093	·9	793·1463	3533

TABLE for Correction of Volumes of Gases—*continued.*

t	760 × $(1 + \delta t)$.	Log. [760 × $(1 + \delta t)$].	t	760 × $(1 + \delta t)$.	Log. [760 × $(1 + \delta t)$].	t	760 × $(1 + \delta t)$.	Log. [760 × $(1 + \delta t)$].
12·0	793·4248	2·899 5058	17·0	807·3518	2·907 0628	22·0	821·2788	2·914 4907
·1	793·7033	6582	·1	807·6303	2126	·1	821·5573	6380
·2	793·9819	8106	·2	807·9089	3624	·2	821·8359	7852
·3	794·2604	9629	·3	808·1874	5121	·3	822·1144	9323
·4	794·5390	2·900 1152	·4	808·4660	6618	·4	822·3930	2·915 0794
12·5	794·8175	2674	17·5	808·7445	8114	22·5	822·6715	2265
·6	795·0960	4196	·6	809·0230	9609	·6	822·9500	3735
·7	795·3746	5717	·7	809·3016	2·908 1104	·7	823·2286	5205
·8	795·6531	7238	·8	809·5801	2598	·8	823·5071	6674
·9	795·9317	8758	·9	809·8587	4092	·9	823·7857	8143
13·0	796·2102	2·901 0277	18·0	810·1372	2·908 5586	23·0	824·0642	2·915 9611
·1	796·4887	1796	·1	810·4157	7079	·1	824·3427	2·916 1079
·2	796·7673	3315	·2	810·6943	8571	·2	824·6213	2546
·3	797·0458	4833	·3	810·9728	2·909 0063	·3	824·8998	4013
·4	797·3244	6350	·4	811·2514	1554	·4	825·1784	5479
13·5	797·6029	7867	18·5	811·5299	3045	23·5	825·4569	6945
·6	797·8814	9384	·6	811·8084	4535	·6	825·7354	8410
·7	798·1600	2·902 0900	·7	812·0870	6025	·7	826·0140	9875
·8	798·4385	2415	·8	812·3655	7515	·8	826·2925	2·917 1339
·9	798·7171	3930	·9	812·6441	9004	·9	826·5711	2802
14·0	798·9956	2·902 5444	19·0	812·9226	2·910 0492	24·0	826·8496	2·917 4265
·1	799·2741	6957	·1	813·2011	1980	·1	827·1281	5728
·2	799·5527	8470	·2	813·4797	3467	·2	827·4067	7190
·3	799·8312	9983	·3	813·7582	4954	·3	827·6852	8652
·4	800·1098	2·903 1495	·4	814·0368	6440	·4	827·9638	2·918 0114
14·5	800·3883	3007	19·5	814·3153	7926	24·5	828·2423	1575
·6	800·6668	4518	·6	814·5938	9411	·6	828·5208	3035
·7	800·9454	6029	·7	814·8724	2·911 0896	·7	828·7994	4495
·8	801·2239	7539	·8	815·1500	2380	·8	829·0779	5954
·9	801·5025	9049	·9	815·4295	3864	24·9	829·3565	7412
15·0	801·7810	2·904 0558	20·0	815·7080	2·911 5347	25·0	829·6350	2·918 8870
·1	802·0595	2066	·1	815·9865	6830	·1	829·9135	2·919 0328
·2	802·3381	3574	·2	816·2651	8312	·2	830·1921	1785
·3	802·6166	5081	·3	816·5436	9794	·3	830·4706	3242
·4	802·8952	6588	·4	816·8222	2·912 1275	·4	830·7492	4699
15·5	803·1737	8095	20·5	817·1007	2756	25·5	831·0277	2·919 6155
·6	803·4522	9601	·6	817·3792	4236	·6	831·3062	7610
·7	803·7308	2·905 1106	·7	817·6578	5716	·7	831·5848	9065
·8	804·0093	2611	·8	817·9363	7195	·8	831·8633	2·920 0520
·9	804·2879	4115	·9	818·2149	8674	25·9	832·1419	1974
16·0	804·5664	2·905 5619	21·0	818·4934	2·913 0152	26·0	832·4204	2·920 3427
·1	804·8449	7122	·1	818·7719	1630	·1	832·6989	4880
·2	805·1235	8625	·2	819·0505	3107	·2	832·9775	6333
·3	805·4020	2·906 0127	·3	819·3290	4583	·3	833·2560	7785
·4	805·6806	1628	·4	819·6076	6059	·4	833·5346	9237
16·5	805·9591	2·906 3129	21·5	819·8861	7535	26·5	833·8131	2·921 0688
·6	806·2376	4630	·6	820·1646	9010	·6	834·0916	2139
·7	806·5162	6130	·7	820·4432	2·914 0485	·7	834·3702	3589
·8	806·7947	7630	·8	820·7217	1960	·8	834·6487	5038
·9	807·0733	9129	21·9	821·0003	3434	26·9	834·9273	6487

TABLE for Correction of Volumes of Gases—*continued.*

t	$760 \times (1 + \delta t)$.	Log. $[760 \times (1 + \delta t)]$.	t	$760 \times (1 + \delta t)$.	Log. $[760 \times (1 + \delta t)]$.	t	$760 \times (1 + \delta t)$.	Log. $[760 \times (1 + \delta t)]$
27·0	835·2058	2·921 7936	28·0	837·9912	2·923 2395	29·0	840·7766	2·924 6807
·1	835·4843	9384	·1	838·2697	3838	·1	841·0551	8246
·2	835·7629	2·922 0832	·2	838·5483	5281	·2	841·3337	9684
·3	836·0414	2279	·3	838·8268	6723	·3	841·6122	2·925 1122
·4	836·3200	3725	·4	839·1054	8165	·4	841·8908	2559
27·5	836·5985	5171	28·5	839·3839	2·923 9606	29·5	842·1693	3995
·6	836·8770	6617	·6	839·6624	2·924 1047	·6	842·4478	5431
·7	837·1556	8062	·7	839·9410	2488	·7	842·7264	6866
·8	837·4341	9507	·8	840·2195	3928	·8	843·0049	8301
27·9	837·7127	2·923 0951	28·9	840·4981	5368	29·9	843·2835	9736
						30·0	843·5620	2·926 1171

Tension of Aqueous Vapour in Millimetres of Mercury, from - 99° to +35° C.

°	m.m.	°	m.m.	°	m.m.	°	m.m.	°	m.m.	°	m.m.
- 9·9	2·096	- 5·4	3·034	- 0·9	4·299	3·5	5·889	8·0	8·017	12·5	10·804
·8	·114	·3	·058	·8	·331	·6	·930	·1	·072	·6	·875
·7	·132	·2	·082	·7	·364	·7	·972	·2	·126	·7	·947
·6	·150	·1	·106	·6	·397	·8	6·014	·3	·181	·8	11·019
·5	·168	- 5·0	·131	·5	·430	3·9	·055	·4	·236	12·9	·090
- 9·4	·186	- 4·9	3·156	- 0·4	·463	4·0	6·097	8·5	·291	13·0	11·162
·3	·204	·8	·181	·3	·497	·1	·140	·6	·347	·1	·235
·2	·223	·7	·206	·2	·531	·2	·183	·7	·404	·2	·309
·1	·243	·6	·231	·1	·565	·3	·226	·8	·461	·3	·383
- 9·0	·261	·5	·257	- 0·0	4·600	·4	·270	8·9	·517	·4	·456
- 8·9	2·280	- 4·4	·283	+ 0·0	4·600	4·5	·313	9·0	8·574	13·5	·530
·8	·299	·3	·309	·1	·633	·6	·357	·1	·632	·6	·605
·7	·318	·2	·335	·2	·667	·7	·401	·2	·690	·7	·681
·6	·337	·1	·361	·3	·700	·8	·445	·3	·748	·8	·757
·5	·356	- 4·0	·387	·4	·733	4·9	·490	·4	·807	13·9	·832
- 8·4	·376	- 3·9	3·414	0·5	·767	5·0	6·534	9·5	·865	14·0	11·908
·3	·396	·8	·441	·6	·801	·1	·580	·6	·925	·1	·986
·2	·416	·7	·468	·7	·836	·2	·625	·7	·985	·2	12·064
·1	·436	·6	·495	·8	·871	·3	·671	·8	9·045	·3	·142
- 8·0	·456	·5	·522	0·9	·905	·4	·717	9·9	·105	·4	·220
- 7·9	2·477	- 3·4	·550	1·0	4·940	5·5	·763	10·0	9·165	14·5	·298
·8	·498	·3	·578	·1	·975	·6	·810	·1	·227	·6	·378
·7	·519	·2	·606	·2	5·011	·7	·857	·2	·288	·7	·458
·6	·540	·1	·634	·3	·047	·8	·904	·3	·350	·8	·538
·5	·561	- 3·0	·662	·4	·082	5·9	·951	·4	·412	14·9	·619
- 7·4	·582	- 2·9	3·691	1·5	·118	6·0	6·998	10·5	·474	15·0	12·699
·3	·603	·8	·720	·6	·155	·1	7·047	·6	·537	·1	·781
·2	·624	·7	·749	·7	·191	·2	·095	·7	·601	·2	·864
·1	·645	·6	·778	·8	·228	·3	·144	·8	·665	·3	·947
- 7·0	·666	·5	·807	1·9	·265	·4	·193	10·9	·728	·4	13·029
- 6·9	2·688	- 2·4	·836	2·0	5·302	6·5	·242	11·0	9·792	15·5	·112
·8	·710	·3	·865	·1	·340	·6	·292	·1	·857	·6	·197
·7	·732	·2	·895	·2	·378	·7	·342	·2	·923	·7	·281
·6	·754	·1	·925	·3	·416	·8	·392	·3	·989	·8	·366
·5	·776	- 2·0	·955	·4	·454	6·9	·442	·4	10·054	15·9	·451
- 6·4	·798	- 1·9	3·985	2·5	·491	7·0	7·492	11·5	·120	16·0	13·536
·3	·821	·8	4·016	·6	·530	·1	·544	·6	·187	·1	·623
·2	·844	·7	·047	·7	·569	·2	·595	·7	·255	·2	·710
·1	·867	·6	·078	·8	·608	·3	·647	·8	·322	·3	·797
- 6·0	·890	·5	·109	2·9	·647	·4	·699	11·9	·389	·4	·885
- 5·9	2·914	- 1·4	·140	3·0	5·687	7·5	·751	12·0	10·457	16·5	·972
·8	·938	·3	·171	·1	·727	·6	·804	·1	·526	·6	14·062
·7	·962	·2	·203	·2	·767	·7	·857	·2	·596	·7	·151
·6	·986	·1	·235	·3	·807	·8	·910	·3	·665	·8	·241
·5	3·010	- 1·0	·267	·4	·848	7·9	·964	·4	·734	16·9	·331

Tension of Aqueous Vapour—*Continued.*

°	m.m.	°	m.m.	°	m.m.	°	m.m.	°	m.m.	°	m.m.
17·0	14·421	20·0	17·391	23·0	20·888	26·0	24·988	29·0	29·782	32·0	35·359
·1	·513	·1	·500	·1	21·016	·1	25·138	·1	·956	·1	·559
·2	·605	·2	·608	·2	·144	·2	·288	·2	30·131	·2	·760
·3	·697	·3	·717	·3	·272	·3	·438	·3	·305	·3	·962
·4	·790	·4	·826	·4	·400	·4	·588	·4	·479	·4	36·165
17·5	·882	20·5	·935	23·5	·528	26·5	·738	29·5	·654	32·5	·370
·6	·977	·6	18·047	·6	·659	·6	·891	·6	·833	·6	·576
·7	15·072	·7	·159	·7	·790	·7	26·045	·7	31·011	·7	·783
·8	·167	·8	·271	·8	·921	·8	·198	·8	·190	·8	·991
17·9	·262	20·9	·383	23·9	22·053	26·9	·351	29·9	·369	32·9	37·200
18·0	15·357	21·0	18·495	24·0	22·184	27·0	26·505	30·0	31·548	33·0	37·410
·1	·454	·1	·610	·1	·319	·1	·663	·1	·729	·1	·621
·2	·552	·2	·724	·2	·453	·2	·820	·2	·911	·2	·832
·3	·650	·3	·839	·3	·588	·3	·978	·3	32·094	·3	38·045
·4	·747	·4	·954	·4	·723	·4	27·136	·4	·278	·4	·258
18·5	·845	21·5	19·069	24·5	·858	27·5	·294	30·5	·463	33·5	·473
·6	·945	·6	·187	·6	·996	·6	·455	·6	·650	·6	·689
·7	16·045	·7	·305	·7	23·135	·7	·617	·7	·837	·7	·906
·8	·145	·8	·423	·8	·273	·8	·778	·8	33·026	·8	39·124
18·9	·246	21·9	·541	24·9	·411	27·9	·939	30·9	·215	33·9	·344
19·0	16·346	22·0	19·659	25·0	23·550	28·0	28·101	31·0	33·405	34·0	39·565
·1	·449	·1	·780	·1	·692	·1	·267	·1	·596	·1	·786
·2	·552	·2	·901	·2	·834	·2	·433	·2	·787	·2	40·007
·3	·655	·3	20·022	·3	·976	·3	·599	·3	·980	·3	·230
·4	·758	·4	·143	·4	24·119	·4	·765	·4	34·174	·4	·455
19·5	·861	22·5	·265	25·5	·261	28.5	·931	31·5	·368	34·5	·680
·6	·967	·6	·389	·6	·406	·6	29·101	·6	·564	·6	·907
·7	17·073	·7	·514	·7	·552	·7	·271	·7	·761	·7	41·135
·8	·179	·8	·639	·8	·697	·8	·441	·8	·959	·8	·364
19·9	·285	22·9	·763	25·9	·842	28·9	·612	31·9	35·159	34·9	·595
										35·0	·827

INDEX.

Absorption apparatus, 199
Acetic acid, 46
Acid, acetic, 46
Acid, rosolic, as indicator, 30
Acid in urine, estimation of, 262
Acids, free, in metallic solutions, 49
Acids, titration of, 45
Acids, combined in neutral salts, 56
Acidimetry, Pettenkofer's, 48
Air, analysis of, 368, 395
Albumen, in urine, estimation of, 262
Albuminoid ammonia, 344
Alkalies, titration of, 37, 85
Alkalimetry, 28
Alkaline earths, 45, 85
Ammonia, 40
Ammonia, apparatus for estimating, 41
Ammonia, combined, 40
Ammonia, albuminoid, 344
Ammonia solution for water analysis, 282
Ammonia in urine, estimation of, 260
Ammoniacal liquor, 42
Ammonia process for waters, 344
Analysis by saturation, 28
Analysis without weights, 4
Analysis by precipitation, 81
Analysis by oxidation and reduction, 61
Analysis without burettes, 5
Analysis of waters, 281
Analysis of sewage, 281
Analytical processes, direct, 26
Analytical processes, indirect, 26
Antimony, estimation of, 182
Apparatus, gas, 302
Apparatus, absorption, 199
Apparatus for water, Bischof's, 295
Arsenious acid and iodine, 79
Arsenic in waters, estimation of, 330
Arsenic, estimation of, 178
Ash, black, analysis of, 89

Balance, the, 4
Baric chloride, normal, 96
Bischof's apparatus for water, 295
Bismuth, estimation of, 168, 416
Bichromate decinormal solution, 68, 70
Black ash, analysis of, 89
Bleaching powder, analysis of, 200
Böhlig's indirect method, 58
Brine, 93
Bromates, analysis of, 203
Bromine, estimation of, 202
Burette, the, 5
Burette, Bink's, 7, 11
Burette, Gay Lussac's, 9, 11
Burette, Geissler's, 11
Burette, Mohr's, 6
Burette stands, 7
Bunsen's gas apparatus, 350

Cadmium, estimation of, 169
Calcium, estimation of, 167
Calibration of gas apparatus, 305
Carbonates, 50
Carbonates, analysis of, 393
Carbonates, metallic, 51
Carbonic acid, 50, 85
Carbonic acid apparatus, 52
Carbonic acid in aërated waters, 54
Carbonic acid in air, 55
Carbonic acid in waters, 53
Carbon, organic, in waters, 293
Carbonic oxide, estimation of, 373
Caustic and carbonated alkalies, mixtures of, 39
Chlorine, estimation of, 83, 199
Chlorine gas, estimation of, 200
Chlorine in waters, estimation of, 322
Chlorates, analysis of, 203
Chlorates, indirect estimation of, 85
Chlorides in urine, 247
Chloro-bromous solution, 113
Chromates, estimation of, 181
Chromic acid and ferrous oxide, 69
Chromium, estimation of, 180
Clark's process for softening water, 343
Coal gas, analysis of, 412
Cobalt, estimation of, 166
Cochineal solution, 30
Combined acids in neutral salts, 56
Copper, estimation by colour titration, 143

Copper, separation of, by galvanic current, 131
Copper titration, methods of, 130—146
Copper ores, technical analysis of, 139
Correction of standard solutions, 34
Cubic centimètre, the, 17
Cupric oxide, pure, 283
Cyanides, alkaline, analysis of, 205
Cyanogen, estimation of, 203

Decimillon, the, 20
Decem, the, 19
Decinormal solution, 21
Distillation apparatus, Bunsen's, 75
Distillation apparatus, Fresenius', 76
Distillation apparatus, Mohr's, 76

Earths, alkaline, 45
Erdmann's float, 14
Estimation of acids in metallic solutions, 49
Eudiometer, the, 351
Evaporation of water for analysis, 294

Ferrous oxide and chromic acid, 69
Ferric iron, estimation of, 119
Ferric salts, titration of, 66
Ferric salts, reduction of, 66, 67, 69, 119
Ferricyanides, estimation of, 206
Ferrocyanides, estimation of, 206
Flask, digesting, 78
Flasks, graduated, 13
Flasks, elastic valve for, 64
Filtering tube, Beales', 98
Free acid in urine, 262

Gas apparatus, Bunsen's, 350
Gas apparatus, Frankland's, 302
Gas apparatus, Frankland and Ward's, 395
Gas apparatus, McLeod's, 397
Gas apparatus, manufacture of, 350
Gas apparatus, improved, 391
Gas apparatus, graduation of, 353
Gas apparatus, calibration of, 305
Gas coal, analysis of, 412
Gas tubes, etching of, 355
Gases, analysis of, 350
Gases, direct estimation of, 365
Gases, explosion of, 379
Gases, indirect estimation of, 365
Gold, estimation of, 184

Hardness in water, 323
Hydrogen, electrolytic, 375
Hydrocyanic acid, estimation of, 204
Hypochlorites, estimation of, 200

Indicators, 28
Indigo, analysis of, 242
Indigo solution for estimating nitrates, 112
Indirect analysis of substances by silver and potassic chromate, 85
Indirect method of analysis, Bohlig's, 58
Instruments for volumetric analysis, 4
Instruments, verification of, 19
Interpretation of water analysis, 331
Iodates, analysis of, 203
Iodine and arsenious acid, 79
Iodine and sodic hyposulphite, 71
Iodine, decinormal solution of, 73
Iodine, free and combined, 194
Iodine, oxidation of, 197
Iodine pure, preparation of, 73
Iron, direct estimation of, by stannous chloride, 119
Iron dyad, estimation of, 115
Iron, estimation of, by colour titration, 123
Iron, estimation of, by hyposulphite, 121
Iron, ferrous, estimation of, 115
Iron in small quantities, estimation of, 123
Iron in silicates, 128
Iron ores, analysis of, 124
Iron ore, chrome, 126
Iron ore, magnetic, 125
Iron ore, Spathose, 125
Iron, triad or tetrad, estimation of, 119

Kainite, 94
Kieffer's solution, 48

Lead, estimation of, 172
Lead in water, estimation of, 330
Lead, refined, assay of, 174
Lime, estimation of, 167
Lime in urine, estimation of, 259
Liquids, expansion and contraction of, 18
Litmus paper, 29
Litmus solution, 28
Litmus, use of, by artificial light, 29

Magnesia in urine, estimation of, 259
Magnesite, use in analysis, 76
Manganese in small quantities, 156
Manganese in spiegeleisen, 157
Manganese ores, decomposition of, by hydrochloric acid, 165
Manganese ores, technical examination of, 160
Manganese, colour titration of, 156
Manganese, estimation of, 153—165
Manganese, oxides, 153
Manures, analysis of, 272—280
Mercury, estimation of, 174—178
Mercurial trough for gas apparatus, 304
Mercurial trough for Sprengel pump, 300
Method of titration, residual, 38

Nessler's solution, preparation of, 281
Nickel, estimation of, 166
Nitrates alkaline, 100
Nitrates and nitrites in waters, 316
Nitrates, estimation by indigo in waters, 320
Nitrates, indirect estimation of, 86
Nitric acid, estimation of, 100—115

Nitric oxide, estimation of, 372
Nitrogen, as ammonia, in waters, &c., 291
Nitrogen, estimation of, 43
Nitrogen, indirect estimation of, 86
Nitrogen, organic, in waters, 293
Nitrites, 417
Normal caustic alkali, 34
Normal hydrochloric acid, 32
Normal nitric acid, 32
Normal oxalic acid, 32
Normal sodic carbonate, 31
Normal solutions, 21
Normal sulphuric acid, 31

Olefiant gas, estimation of, 373
Ores, copper, technical analysis of, 139
Ores, iron, analysis of, 124
Ores, manganese, 160
Ores, sulphur, analysis of, 208
Organic carbon in waters, 293
Organic nitrogen in waters, 293
Oxygen gas, estimation of, 372
Oxygen pipette, 308

Pearlash, 94
Permanganate analyses, calculation of, 67
Permanganate, fractional titration with, 66
Permanganate solution, 62
Permanganate solution, precautions in using, 65
Permanganate solution, titration of, 63, 64
Pettenkofer's acidimetry, 48
Phosphates, analysis of, 217
Phosphates, Fresenius, Neubauer, and Luck's method of assaying, 276
Phosphates in urine, 256
Phosphoric acid, estimation of, 217—233
Phosphoric acid, separation of, 224
Pinchcocks, various, 12
Pipette, oxygen, 308
Pipette, the, 12
Potash, caustic, raw, 94
Potash, indirect estimation of, 86
Potash in urine, estimation of, 263
Potash, volumetric estimation of, 94
Potassic chromate as indicator in chlorine analysis, 84
Potassic cyanide, analysis of, 205
Potassic iodide, solution for absorption, 77
Precipitation analysis, 81
Principles of volumetric analysis, 1
Processes, direct, 26
Processes, indirect, 26
Pump, Sprengel, 299
Pyrites, analysis of, 208

Reagents, preparation of, for water analysis, 281
Reading of graduated instruments, 14
Rosolic acid as indicator, 30
Rules for percentages, 23

Salt, cake, 92
Salt, raw, 93
Salt, decinormal solution of, 82
Samples of water, how to collect, 289
Septem, the, 20
Sewage analysis, 281
Silver, assay of, 187
Silver, assay, Gay Lussac's process, 187
Silver, estimation of, 185
Silver solutions, assay of, 185
Silver, decinormal solution of, 82
Soda ash, commercial analysis of, 88
Soda and potash, mixed caustic, 92
Soda, indirect estimation of, 86
Soda liquor, analysis of, 89
Soda in urine, estimation of, 263
Sodic arsenite, solution, 79
Sodic chloride, decinormal, 82
Sodic hyposulphite, solution of, 73
Solutions, decinormal, 21
Solutions, empirical, 25
Solutions, standard, expansion and contraction of, 18
Solutions, normal, 21
Solution, Kieffer's, 48
Solutions, preservation of, 25
Soap, titration of, 93
Soils, analysis of, 265—272
Solid matter in waters, 316
Spiegeleisen, 117
Spiegeleisen, manganese in, 157
Sprengel pump, 299
Standard soap solution, 288
Standard solutions, correction of, 34
Standard water for hardness, 288
Starch paper, 80
Starch liquor, 74
Stannous chloride, solution of, 70
Stannous chloride, as reducing agent, 69
Steel, analysis of, 117
Substances, distillation of, with hydric chloride, 75
Sugar, estimation of, 237
Sugar in urine, 258
Sulphates in urine, 257
Sulphides, alkaline, estimation of, 214
Sulphites, estimation of, 214
Sulphur, estimation of, 208
Sulphur in coal gas, estimation of, 213
Sulphur in pyrites, estimation of, 210
Sulphuric acid, direct precipitation, 98
Sulphuric acid, estimation of, 95
Sulphurous acid, estimation of, 214
Superphosphates, 231
Superphosphates containing ammonia, 232
Superphosphates containing iron and alumina, 233
Sulphuretted hydrogen, estimation of, 215
Sulphuretted hydrogen waters, analysis of, 216
Suspended matter in waters, 321
System, the gramme, 17
Systematic volumetric processes, 20

Table, systematic for acids and alkalies, 44
Tannic acid, estimation of, 233
Tannin in tea, estimation of, 236
Tea, tannic acid in, 236
Test mixer, 16
Tin, estimation of, 169
Titration of permanganate solution, 63
Titration of permanganate with oxalic acid, 64
Titration of permanganate with iron, 64
Titration, residual methods of, 38
Titration of acids, 45
Titration of alkalies, 37
Total solid matter in waters, 316
Turmeric paper, 30

Uranium, estimation of, 171, 418
Uranium solution for phosphates, 220, 231
Uranium residues, recovery of, 418
Urea, estimation of, as nitrogen gas, 253
Urea, estimation of, 250
Uric acid, estimation of, 259
Urine, analysis of, 246

Valve, elastic, for flasks, 64
Verification of graduated instruments, 19
Volumetric analysis, principles of, 1
Volumetric analysis, methods of, 3

Water analysis, 281
Water analysis, interpretation of, 331
Water analysis by the ammonia process, 344
Water free from ammonia, 282
Water residues, combustion of, 301
Water, softening of, by Clark's process, 343
Weights and measures, 16

Zinc, methods of titration, 146—153, 414

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THE

CHEMICAL ANALYSIS OF IRON

A COMPLETE ACCOUNT OF ALL THE BEST
KNOWN METHODS

FOR THE

*Analysis of Iron, Steel, Pig-Iron, Iron Ore, Limestone,
Slag, Clay, Sand, Coal, Coke, and Furnace
and Producer Gases*

BY

ANDREW ALEXANDER BLAIR

GRADUATE UNITED STATES NAVAL ACADEMY, 1866; CHIEF CHEMIST UNITED STATES BOARD APPOINTED TO
TEST IRON, STEEL, AND OTHER METALS, 1875; CHIEF CHEMIST UNITED STATES GEOLOGICAL
SURVEY AND TENTH CENSUS, 1880; MEMBER AMERICAN PHILOSOPHICAL
SOCIETY, ETC.

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TO

MY WIFE

WITHOUT WHOSE ASSISTANCE IT WOULD NEVER HAVE
BEEN WRITTEN

THIS VOLUME
IS
Dedicated

PREFACE TO THE FOURTH EDITION.

THE number of improved methods available, the use of new materials in technical work, and the general advance in chemical knowledge necessitated so many changes that in preparing the fourth edition of this work I decided to rewrite it entirely. In doing this I have substituted chemical terms for formulas in the text, omitted the marginal notes, and changed the nomenclature to coincide with that in general use. I hope that these changes will recommend themselves to the users of the book. The prompt and generous response to requests for information from members of my profession is shown in the foot-notes.

The entire labor of proof-reading and index-making has, by my enforced absence, been thrown on my friend and co-worker, Mr. J. Edward Whitfield, to whom this brief acknowledgment is but a poor indication of the weight of my obligation.

BORDIGHERA, January, 1901.

PREFACE TO THE THIRD EDITION.

SUCH changes as were necessary to bring the methods for the determination of the various elements in accord with the present state of the science have been made in this edition.

The method for the "Volumetric Determination of Phosphorus in Steel" is that worked out by the Sub-Committee on Standards of the International Steel Standards Committee, and as such is merely tentative. Its publication here is not official, but through the courtesy of the committee it is placed before the profession in the hope that criticism may confirm its value or point out its errors. The modifications in the method for the determination of sulphur in pig-iron are improvements, but no method is perfectly satisfactory. Two new methods for the determination of carbon are given, and some modifications of Volhard's method for the determination of manganese in high grade manganese ores are introduced.

Many minor changes have been made, and it is hoped that this edition may meet the same cordial reception as the two former.

LABORATORY OF BOOTH, GARRETT & BLAIR,
PHILADELPHIA, September, 1896.

PREFACE TO THE SECOND EDITION.

IN preparing the second edition of this book I have tried to correct the mistakes that were apparent in the first edition, and to add such matter as the advance in analytical chemistry seemed to justify. In effecting the first of these objects I have been aided by such kindly criticism as the profession and reviews offered me, and in the second by the advice and assistance of many of my fellow-workers. Among others my thanks are due to Messrs. Maunsel White and A. L. Colby, of the Bethlehem Iron Company; Mr. Clemens Jones, of the Thomas Iron Company; Mr. E. F. Wood, of the Homestead Steel-Works; Mr. T. T. Morrell, of the Cambria Iron Company; Mr. H. C. Babbitt, of the Wellman Steel Company; Prof. F. W. Clarke, Chief Chemist U. S. Geological Survey; Mr. J. E. Stead, of Middlesborough, England; and Mr. J. Edward Whitfield, of Philadelphia.

It will be seen that the "Table of Atomic Weights" has been revised; the latest and most reliable values for the elements are given, and the "Table of Factors" has been changed to correspond to these values.

LABORATORY OF BOOTH, GARRETT & BLAIR,
PHILADELPHIA, June, 1891.

PREFACE TO THE FIRST EDITION.

THE various methods for the analysis of iron and steel, as well as the descriptions of special apparatus to facilitate the performance of the analytical work, are so widely distributed through transactions of societies, journals, reviews, periodicals, and works on general analytical chemistry that only the possessor of a chemical library can command the literature of the subject. It is my object in the following pages to bring within the compass of a single volume, as nearly as possible, all the methods of real value to the iron analyst, and in doing this to give the credit of originality for the different methods and improvements to the proper persons. In many cases this has been very difficult, and I shall be glad to have any mistake brought to my attention.

This work presupposes some knowledge of general and analytical chemistry, and some practical experience in laboratory work and manipulation, as it is intended to be a guide for the student of iron chemistry only. For such persons the details of the descriptions of the methods will, I hope, often prove of great assistance. With very few exceptions, these descriptions are the results of my own experience in the use of the methods, and the details are those that seemed to me to be of importance in their practical performance. Many of the special forms of apparatus are of my own contrivance; they have proved extremely useful to me, and I hope may facilitate in some cases the work of iron chemists, to whom often very little is given and of whom very much is required.

CONTENTS.

PAGE

APPARATUS 11

Apparatus for the Preparation of the Samples 11

General Laboratory Apparatus 18

REAGENTS 37

Acids and Halogens, 38. Gases, 42. Alkalies and Alkaline Salts, 44. Salts of Alkaline Earths, 51. Metals and Metallic Salts, 53. Reagents for Determining Phosphorus, 59.

METHODS FOR THE ANALYSIS OF PIG-IRON, BAR-IRON, AND STEEL 60

Determination of Sulphur. By evolution as Hydrogen Sulphide. *Absorption by alkaline solution of lead nitrate*, 60; *by ammoniacal solution of cadmium sulphate*, 63; *by ammoniacal solution of silver nitrate*, 63. *Absorption and oxidation by bromine and hydrochloric acid*, 64; *by potassium permanganate*, 65; *by hydrogen peroxide*, 65. By oxidation and solution, 66. Bamber's method for pig-iron, 67. Special precautions in the determination of sulphur in pig-irons, 67. Rapid Methods. Volumetric determination by iodine, 68.

Determination of Silicon, 72. By solution in nitric and hydrochloric acids, 72; in nitric and sulphuric acids, 73. By volatilization in a current of chlorine gas, 73. Rapid Method, 77.

Determination of Slag and Oxides, 78. By solution in iodine, 78. By volatilization in a current of chlorine gas, 80.

Determination of Phosphorus, 80. The acetate method, 80. *When titanium is present*, 85. The molybdate method, 88. The combination method, 91. *When titanium is present*, 92. Rapid Methods, 92. Volumetric method, 92. Alkalimetric method, 104. Direct weighing of the phosphomolybdate, 106.

Determination of Manganese, 108. The acetate method, 108. *General remarks on the acetate method*, 112. The nitric acid and potassium chlorate method (Ford's), 113. *Steels containing much silicon*, 115. Pig-iron, 115. Spiegel and ferro-manganese, 115. Rapid Methods, 116. Volumetric methods. *Volhard's method*, 116. *Williams's method*, 118. *Deshays's method*, 121. *Vanier's modification*, 122. *Pattinson's method* (*for spiegel and ferro-manganese*), 123. The color method (for steel), 124.

Determination of Carbon, 126. Total Carbon, 126. Direct combustion in a current of oxygen, 128. Combustion with lead chromate and potassium chlorate, 129; with cupric oxide in a current of oxygen, 131; with potassium bisulphate, 132. Solution and oxidation in sulphuric, chromic, and phosphoric acids, the volume of the carbonic acid being measured, 137; the carbonic acid being weighed, 140. Volatilization of the iron in a current of chlorine, and subsequent combustion of the residue, 142. Volatilization of

PAGE
the iron in a current of hydrochloric acid gas, and subsequent combustion of the residue, 148. Solution in potassium-cupric chloride, filtration, and weighing or combustion of the residue, 148. *Modification of Job and Davies*, 160. Repeated use of potassium-cupric chloride for the solution of steel, 164. Solution in cupric chloride, and combustion of the residue, 165. Solution in iodine or bromine, and combustion with lead chromate, or weighing, of the residue, 165. Solution on fused silver chloride, and combustion of the residue, 166. Solution in cupric sulphate, filtration, and combustion of the residue in a current of oxygen, 167. Solution in cupric sulphate, and oxidation of the residue by chromic and sulphuric acids, 168. Solution in dilute hydrochloric acid by the aid of an electric current, and combustion of the residue, 168.

DETERMINATION OF GRAPHITIC CARBON 169

DETERMINATION OF COMBINED CARBON, 170. Indirect method, 170. Direct method (color method), 170.

DETERMINATION OF TITANIUM, 179. By precipitation, 179. By volatilization, 180.

DETERMINATION OF COPPER 180

DETERMINATION OF NICKEL AND COBALT, 183. The acetate method, 183. The ether method, 186.

DETERMINATION OF CHROMIUM, 188. The ether method, 189. Volumetric method, 189. *Barba's modification*, 190.

DETERMINATION OF ALUMINUM, 191. Stead's method, 191. Carnot's method, 192. Ether method, 193.

DETERMINATION OF ARSENIC 194

DETERMINATION OF TIN 195

DETERMINATION OF TUNGSTEN 196

DETERMINATION OF VANADIUM 197

DETERMINATION OF MOLYBDENUM, 199. In ferro-molybdenum, 200.

DETERMINATION OF NITROGEN 200

DETERMINATION OF IRON 203

METHODS FOR THE ANALYSIS OF FERRO-CHROME, FERRO-SILICON, AND FERRO-TITANIUM 205

DETERMINATION OF CARBON 205

DETERMINATION OF SULPHUR 205

DETERMINATION OF SILICON 206

DETERMINATION OF PHOSPHORUS, 207. In ferro-chrome, 207. In ferro-silicon, 207. In ferro-titanium, 208.

DETERMINATION OF MANGANESE 208

DETERMINATION OF CHROMIUM, 208. Gravimetric method, 208. Volumetric method, 209.

DETERMINATION OF IRON 209

METHODS FOR THE ANALYSIS OF IRON ORES 210

Remarks on sampling, 210. Determination of hygroscopic water, 211. Determination of total iron, 212. Methods of standardizing the solutions, 217. Determination of ferrous oxide, 221. Of sulphur, 225. Of phosphoric acid, 227. Of titanic acid, 229. Of manganese, 230. *Pattinson's method*, 232. Determination of manganese dioxide, 233. *Bunsen's method*, 234. *By ferrous sulphate*, 235.

PAGE
DETERMINATION OF SILICA, ALUMINA, LIME, MAGNESIA, MANGANESE OXIDE, AND BARYTA 236
DETERMINATION OF SILICA, 244. Separation of alumina and ferric oxide, 245.
DETERMINATION OF NICKEL, COBALT, ZINC, AND MANGANESE, 248; of copper, lead, arsenic, and antimony, 249; of the alkalies, 252; of carbonic acid, 253; of combined water and carbon in carbonaceous matter, 255; of chromium, 258; of tungsten, 260; of vanadium, 260; of the specific gravity, 260.
METHODS FOR THE ANALYSIS OF LIMESTONE 262
METHODS FOR THE ANALYSIS OF CLAY 266
METHODS FOR THE ANALYSIS OF SLAGS 271
METHOD FOR THE ANALYSIS OF FIRE-SANDS 275
METHODS FOR THE ANALYSIS OF COAL AND COKE 276
Proximate analysis, 276. Determination of volatile combustible matter, 277. Of ash, 278. Of fixed carbon, 278. Of sulphur, 278. *By Eschka's method*, 279.
DETERMINATION OF PHOSPHORIC ACID, 281. Ultimate analysis, 282. Heating effect, 283.
METHODS FOR THE ANALYSIS OF GASES 285
Collecting samples, 285. Reagents for the pipettes, 288. Analysis of the sample, 290.
DETERMINATION OF CARBONIC ACID, 292. Of oxygen, 292. Of carbonic oxide, 292. Of hydrogen, 293. Of methane, 295. Of nitrogen, 297. Example of calculation, 298.
TABLES 299
Table I. Atomic weights of the elements, 299. Table II. Table of factors, 300. Table III. Percentages of phosphorus and phosphoric acid for each milligramme of magnesium pyrophosphate, 302. Table IV. Tension of aqueous vapor, 303. Table V. Table for reducing volumes of gases to the normal state, 304.
INDEX 311

THE CHEMICAL ANALYSIS OF IRON.

APPARATUS.

THE speed and facility with which results may be obtained, and often the accuracy of these results, are dependent upon various mechanical appliances as well as upon the skill of the analyst. These appliances will be considered under separate heads.

APPARATUS FOR THE PREPARATION OF THE SAMPLES.

For crushing iron ores, a mortar and pestle, such as are ordinarily used, have caused much trouble. In breaking up hard ores the wear, especially on the pestle, is considerable, and the particles of cast iron may cause the sample to yield too high a result in the determination of metallic iron. Of course, in non-magnetic ores these particles may be removed with a magnet, but in the case of magnetic or partly magnetic ores this cannot be done, and a hardened steel mortar and pestle should be used. The sample should be broken to about pea size, well mixed, and quartered, this quarter broken still finer, and mixed and quartered in the same way until the resulting portion is small enough to be bottled. The final grinding can be best done on a chilled-iron plate with a hardened steel muller. Except with unusually refractory ores, further grinding is unnecessary, but with such ores the final grinding must be in an agate mortar. In large laboratories and where many ores are analyzed, arrangements such as are shown in the accompanying sketches will prove very useful. Fig. 1 shows a steel mortar, the pestle worked by power, and a chilled plate and muller.

A is the mortar; B, a wooden stem in which the pestle fits. The cams H fit on the shaft and raise the pestle by means of the tappets *a*, which are faced with raw hide. An iron hoop shrunk on the mortar has a ring, in which is fastened the lower block of the pulley D; the upper block is attached to a traveller, E. When in use the mortar is covered with a leather cap, which prevents the pieces of ore from flying out of the mortar. To transfer the powdered ore to the chilled plate F, remove the leather cap, raise the pestle clear of the mortar, and fasten it up by a hook from the framework to the tappet *a*. Raise the mortar by pulling the fall from the upper block and fastening the hook in its end into a ring at the lower block. By means of the traveller, run the mortar over the plate and turn the ore out. After quartering the sample down, finish the grinding on the chilled plate with the muller C. The sheet-iron troughs G serve to catch any ore that falls from the plate. In some laboratories a small Blake crusher is used for crushing the ore, but it is more liable to get out of order, and is not so easily cleaned as the mortar and pestle. Fig. 2 shows an arrangement for facilitating the final grinding in the agate mortar, in which the pestle is rotated by a Stow flexible shaft.

FIG. 1.

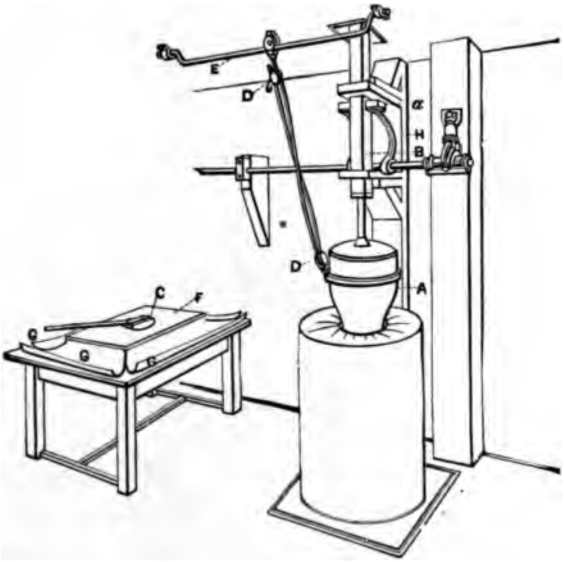


Fig. 2.

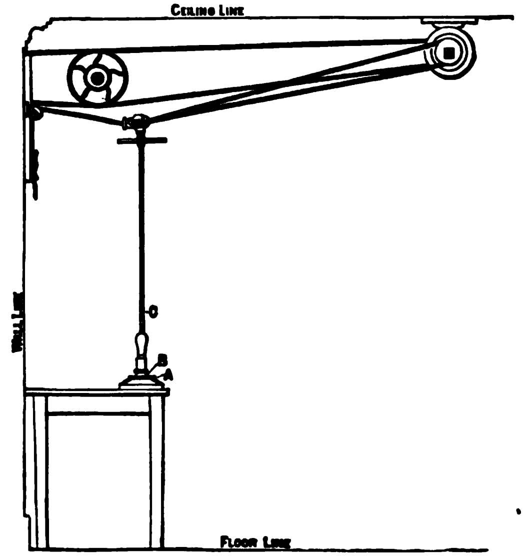
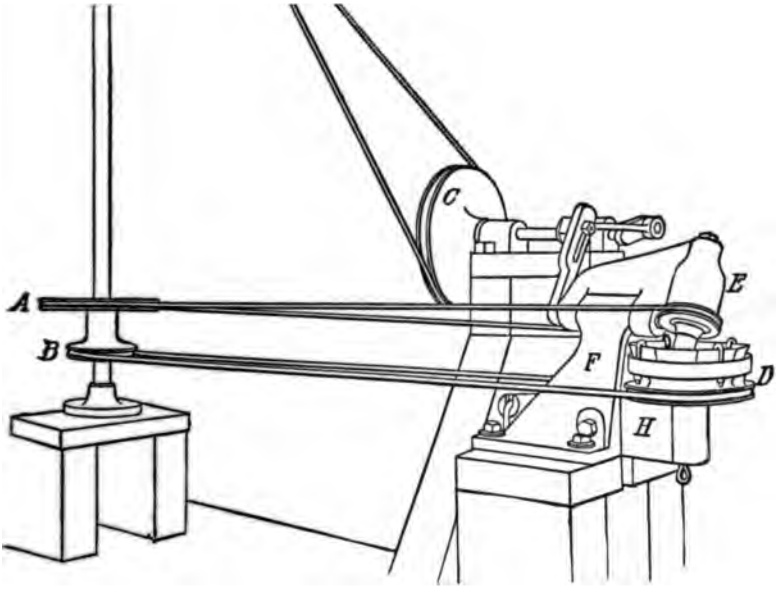


Fig. 3.



The apparatus shown in Fig. 3, designed by Mr. Maunsel White, has been in use several years at the chemical laboratory of the Bethlehem Iron Company, and has worked very satisfactorily. The power is applied from an overhead countershaft not shown in the cut. The lower portion of the vertical shaft carries two horizontal pulleys, A and B; these pulleys are connected, as shown, with the spindle carrying the pestle and with the circular box D, in which the mortar is securely fastened by four claw-bolts, which may be seen in the drawing.

The piece D is made with a spindle which extends down into a bearing in the supporting piece H. The piece H, which may be called a lever, is secured to the frame F by a bolt which passes through it, and around which it can be turned through an angle sufficient to permit of the easy emptying of the mortar without displacing the belt. A groove at the farther end of H, as shown, carries a weighted rod which supplies the pressure of the mortar against the pestle. The weights are made movable so that the pressure can be varied for special cases.

The agate pestle is secured in a brass spindle with a grooved collar for carrying the belt; this spindle revolves in a bored socket in the piece E, and is secured from dropping out by means of a small nut, shown at the top of the piece. The piece E is connected to the frame F by a circular bolt, the end of which is supplied with an arm for rocking the piece E; this obtains by fastening the bolt with dowel-pins where it passes through the piece E while free to move in the frame F. The pulley C is run from the countershaft, and revolves a small shaft whose end carries a crank connected by a short rod to the bolt-arm of the piece E, and supplies the power and means for the rocking motion.

It will now be seen that while the mortar revolves, the pestle, revolving more rapidly, sweeps across the face of the mortar by the rocking motion of the piece E, thus constantly changing the material between the grinding surfaces.

In taking samples of iron or steel, a perfectly clean dry drill should be used, and the utmost care taken to prevent grease, oil, or dirt of any kind from getting in the sample. With bar-iron or steel the scale on the outside of the piece should be removed as carefully as possible, the first drillings from each hole thrown away, and the remainder thoroughly mixed and placed in a perfectly clean dry bottle. Fig. 4 shows a convenient form of drill-press for the purpose. A half-inch Morse twist-drill is the best for general use. In taking samples of pig-iron, the loose sand should be carefully removed from the outside of the pig and a piece of stout paper wrapped around it to prevent the sand and slag from the outside getting mixed with the clean drillings, which are received on a piece of glazed paper turned up at the edges (Fig. 4). Drillings from pig-iron can be best mixed by rubbing them up in a small porcelain mortar. At blast-furnaces, to save the trouble of breaking pieces from the pigs the arrangement shown in Fig. 5 is very convenient, as half a pig can be placed in the press. The framework is securely bolted to the table on which the press stands, and the pig is secured by means of the iron clamps. By removing the pieces of wood under the pig it is lowered so that two or three holes can be bored in different parts of the face of the pig to get an average. By taking one pig from the first bed, one from the last, and one from an intermediate bed,

FIG. 4.

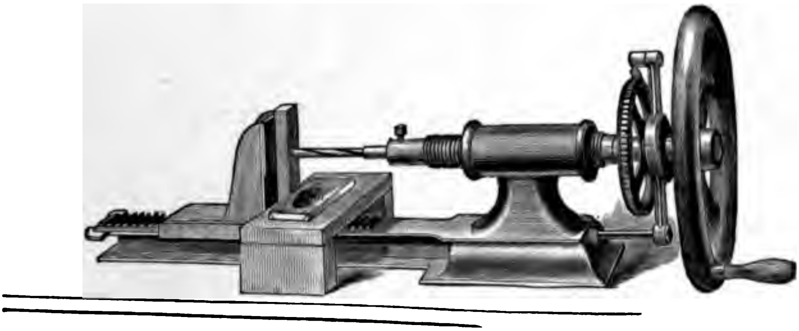
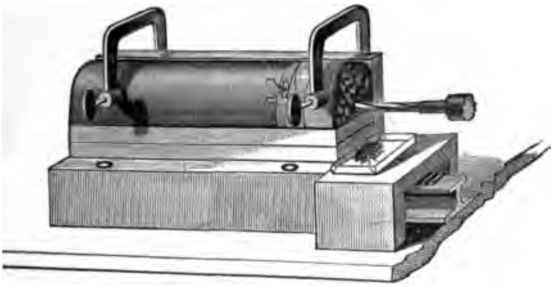


FIG. 5.

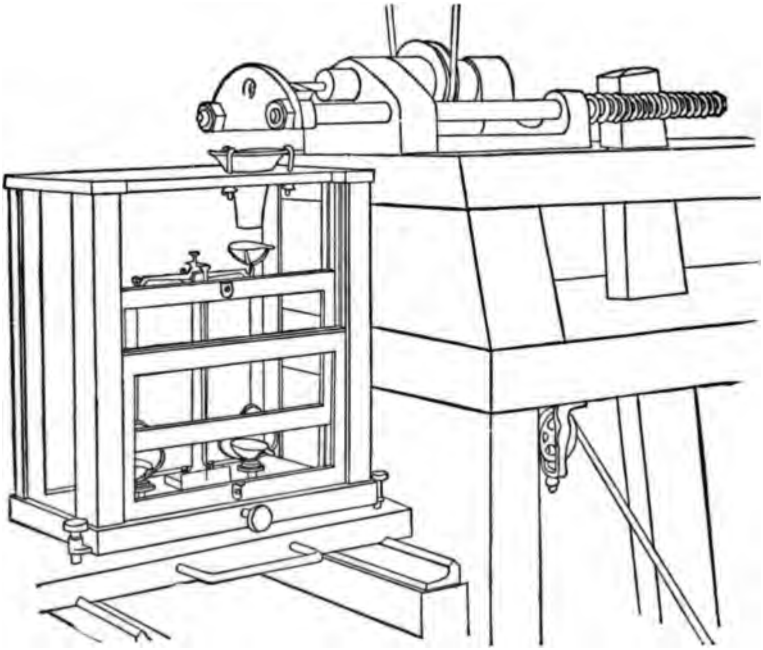


a good average of each cast may be obtained. When the ore varies, or when mixtures of different ores are used, these precautions are very necessary to get a sample that will really represent an average of the cast.

Drillings from large ingots must be taken by means of an ordinary brace.

Fig. 6 shows an apparatus for the drilling and weighing of samples of steel for colorimetric carbon or other rapid determinations, designed by

FIG. 6.



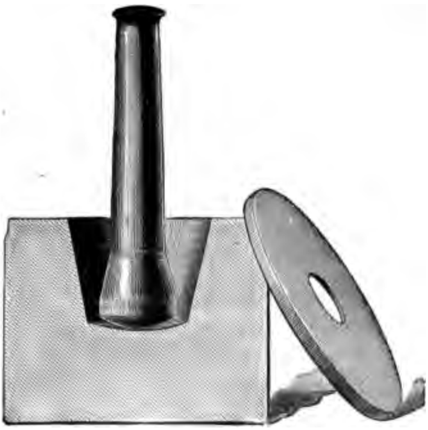
Mr. Maunsel White, and in use at the laboratory of the Bethlehem Iron Company. The drill is mounted above the balance, the point of the drill directly overhanging the balance-pan. The piece to be drilled is placed against the semicircular plate carried by the two rods that pass through the drill-frame; on the rear end of each rod is a coiled spring which supplies the pressure necessary for drilling. The rear ends of the rods are held together by a tie-piece, which is connected to a lever operated by the foot, so that the rods and plate can be forced forward for the reception of the piece to be drilled.

The balance is supplied with an overhead pan which receives the drillings guided to it through the funnel fixed in the top of the balance-case for this purpose. When the pan falls, showing that sufficient sample has been drilled, pressure is applied to the lever by the foot and the piece taken out. The balance-case rests upon an iron plate grooved on the bottom ; these grooves engage with guides screwed to the table and permit the balance-case to be pulled forward, which facilitates the cleaning of the funnel from all clinging particles. This operation is done with a camel's-hair brush or a feather. A magnet is run around in the lower pans to guard against the chance of falling particles interfering with the accuracy of the weights. The upper door of the balance-case is then lowered into the position shown in Fig. 6, which gives free access to the upper pan containing the sample. The sample is now accurately weighed, the pan lifted out, and the drillings transferred to the test-tube.

The use of a ¼-inch twist-drill has been adopted and found to give good results. The pans and funnel are aluminum and the bearings agate; the beam is short, 5½ inches in length, in consequence of which the weighing is done rapidly.

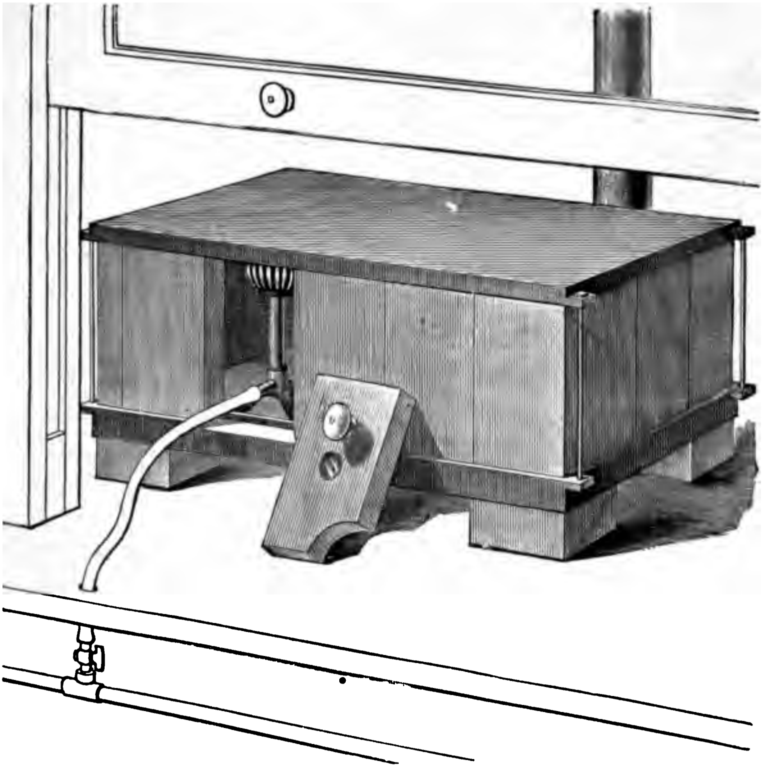
In taking samples of spiegel or of white-iron, small clean pieces from a number of pigs should be taken and powdered in a hardened steel mortar. The mortar shown in the sketch (Fig. 7) is forged from high carbon steel, hardened, and the temper drawn from the outside. This makes the mortar both hard and tough. The sheet-iron cover prevents the pieces from flying. The face of the pestle is very hard, and the handle comparatively soft, so that it will not break when struck by the hammer.

FIG. 7.



In taking samples for analysis, when the method used requires the sample to be in a fine state of subdivision, the very fine part of the sample should never be separated from the coarser particles by a sieve or screen, but the sample should be mixed thoroughly, and a portion, fine and coarse together, taken and powdered, so that all may pass through the sieve.

Fig. 8.

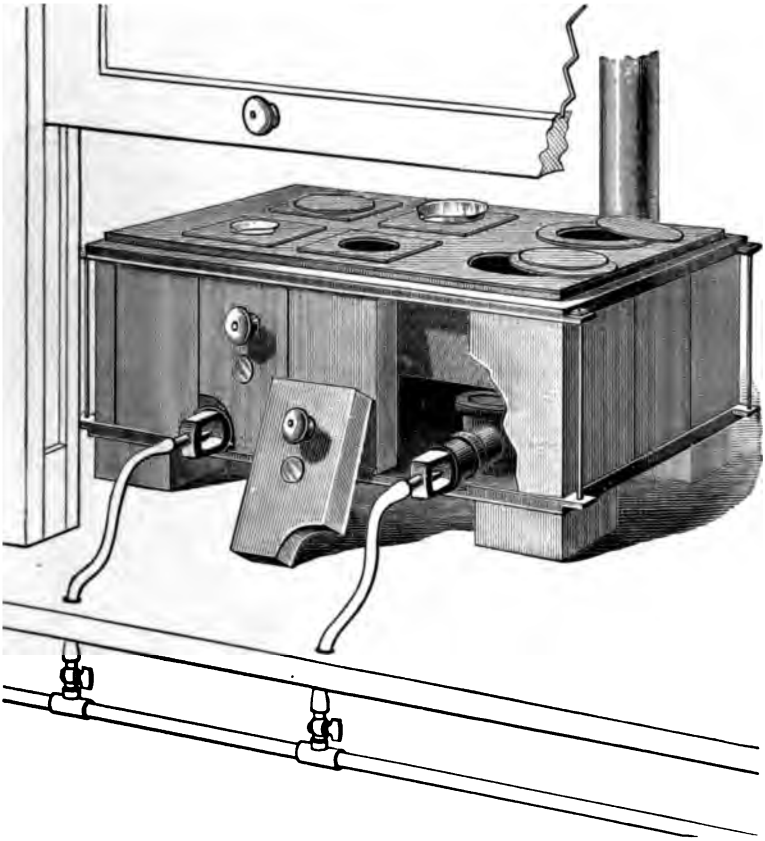


GENERAL LABORATORY APPARATUS.

Hot Plate and Air-Bath.

Fig. 8 shows a very convenient form of hot plate, and Fig. 9 an air-bath. This air-bath is made from an ordinary cast-iron sink, which is supported on fire-bricks. The top is of asbestos board, with a piece of sheet-iron underneath to strengthen it. The holes are large enough to take the largest-sized beakers, while the smaller beakers are supported by asbestos rings. An ordinary gas-regulator or governor, which supplies

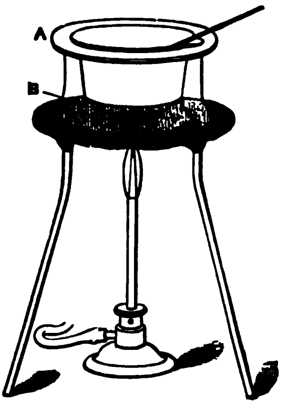
FIG. 9.



the gas at a constant pressure, keeps the temperature sufficiently uniform. Evaporations may thus be effected with great saving of time and with little danger of loss by spirting. The products of combustion of the gas are carried off by a separate flue, and the sulphuric acid formed does not come in contact with the solutions in the baths.

The hot plate is generally used instead of a sand-bath, the surface of the iron being kept clean and free from rust by an occasional coat of stove-polish. Evaporations on the hot plate may be hastened by standing the beaker containing the solution inside another beaker with the bottom cut off. Beakers may readily be cut in this way by starting a crack and leading it around with a red-hot iron or glass rod. For evaporating solutions in capsules or dishes a beaker cut off in this way and placed on a tripod covered with wire gauze, as shown in Fig. 10, may be used with great advantage. The capsule is supported on an asbestos ring, A, the bottom being about ½ inch (12 mm.) from the wire gauze. A piece of thin asbestos board, B, about ¾ inch (18 mm.) in diameter, rests on the gauze and covers the point of the flame of the Bunsen burner, and, by throwing the heat more on the sides of the capsule, tends to prevent spirting when the solution in the capsule gets thick and pasty.

FIG. 10.

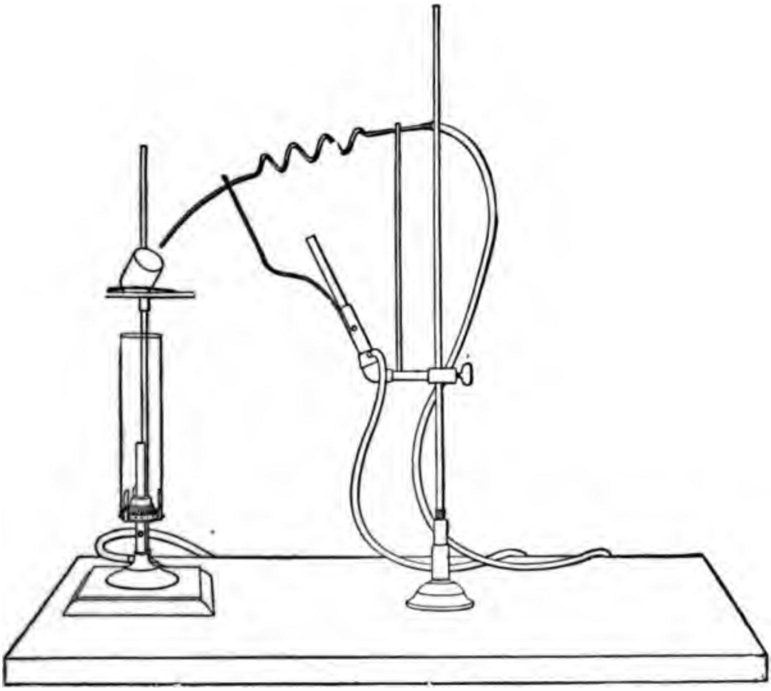


Apparatus for Hastening Evaporations.

The little piece of apparatus shown in Fig. 11 was designed by Mr. J. E. Whitfield and is most useful in hastening evaporations. It consists of a platinum tube $\frac{3}{16}$ of an inch in diameter, coiled above the burner to present more heating surface, through which passes a blast of air. As the platinum tube and Bunsen burner are both supported on the arm of the stand, the level of the tube may be made to accommodate itself to a crucible on a stand, to a capsule on a tripod (Fig. 10), or to a beaker on the air-bath. In the treatment of the insoluble residues from ores by hydrofluoric and sulphuric acids it is quite invaluable, as it not only hastens the evaporation but prevents loss by spirting.

The blast of hot air breaks the bubbles on the surface of the liquid, and when properly directed it gives the liquid a rotary motion that tends to throw onto the sides of the crucible any particles of the liquid thrown up by the bubbles. The amount of heat that can be applied to a crucible under these circumstances, without causing loss, is really surprising. It is equally useful when evaporating solutions in beakers on the air-bath or hot plate. In laboratories where a blast of air is always at command, the principle may be applied in many ways for hastening evaporations.

FIG. 11.



Even a cold blast of air from a drawn-out glass tube directed on the surface of a liquid hastens the evaporation very materially.

Igniting Precipitates.

For ignitions, a Bunsen burner with a ring to regulate the supply of air, provided with an ordinary glass chimney, as shown in Fig. 12, is most convenient. By shutting off the air entirely a very low heat may be obtained, which is not rendered variable by air-currents, and the heat of the full flame of the burner is increased by the greater draft caused by the chimney and the perfect steadiness of the flame. By using a small platinum rod or wire to support the cover of the crucible, as shown in Fig. 12, a gentle current is induced in the crucible, which, while it greatly facilitates burning off carbon, is not sufficiently strong to cause loss by carrying off even the lightest ash. The crucible may also be inclined on its side, as in Fig. 13, the heat in this case being applied near the top of the crucible. Fig. 14 shows an easy method of fitting a chimney to a Bunsen burner by means of a cork and an ordinary Argand chimney-holder. When a higher temperature than that obtainable by a Bunsen burner is required, a blast-lamp, worked by a foot-bellows, by a water-blast, or by a small blower, is used.

FIG. 12.

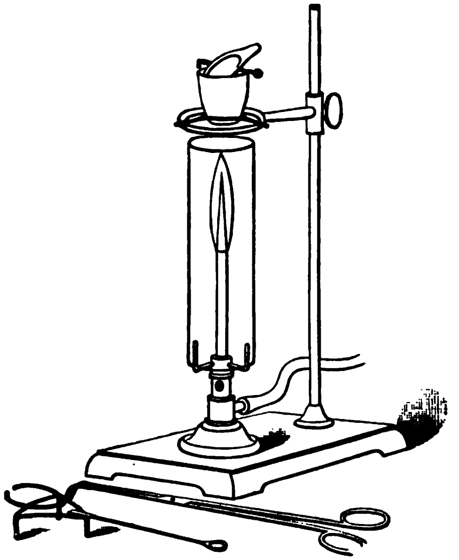


FIG. 13.

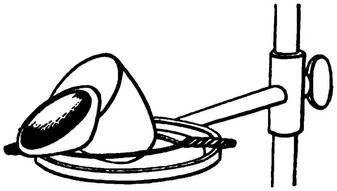
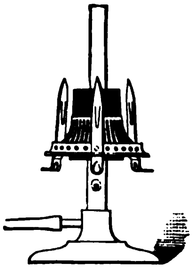


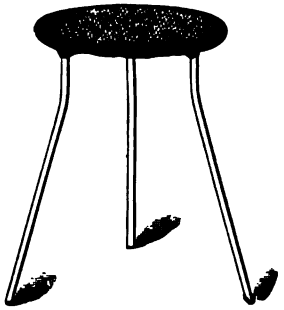
FIG. 14.



Tripods.

The most convenient arrangement for heating liquids in beakers, flasks, etc., is the iron tripod (Fig. 15). It consists of a cast-iron ring with three legs of heavy iron wire ¼ inch (6 mm.) in diameter. The ring is covered with brass wire gauze, 40 meshes to the inch, which can be replaced when it is burned out, but which lasts a long time. The vertical height of the tripod is about 7½ inches (191 mm.). A very convenient form of burner is the Finkner ratchet-burner, as the flame can be raised or lowered by means of the ratchet on the burner, thus avoiding the necessity of reaching back over the table to the gas-cock. As the air and gas are both turned off at once, there is less danger of the flame blowing out when it is turned very low.

FIG. 15.



Gasoline and Alcohol Lamps.

When illuminating gas is not obtainable for heating purposes, recourse must be had to gasoline or alcohol. If a gasoline gas machine is available it furnishes a fair substitute for ordinary illuminating gas, but special burners must be used. These will be found described in any dealer's catalogue. Sometimes, however, it is necessary to depend on gasoline alone as a source of heat, and in this event the best burner for general use is the Dangler lamp, which can be used for heating solutions and also for making ignitions and for fusions. This lamp is made on the principle of the plumber's torch or melting-pot.

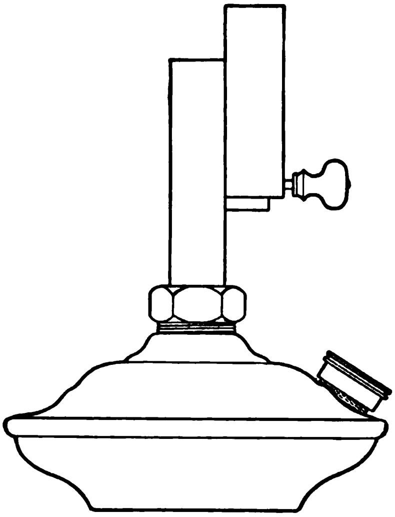
Alcohol is too expensive for general use for heating purposes, but for fusions for the determination of sulphur its use is advisable on account of the presence of sulphur compounds in gas. There are many patterns of alcohol lamps, among others Barthel's lamp of the form shown in the cut (Fig. 16) may be mentioned.

Muffles.

Some analysts prefer to make ignitions in a muffle, and where no gas is available it certainly offers many advantages.

Any good form of muffle furnace heated by gasoline, coke, or coal may be used for this purpose, but the muffle should not be less than 4 or 5 inches in height. The waste heat may be used for a hot plate or an air-bath.

FIG. 16.

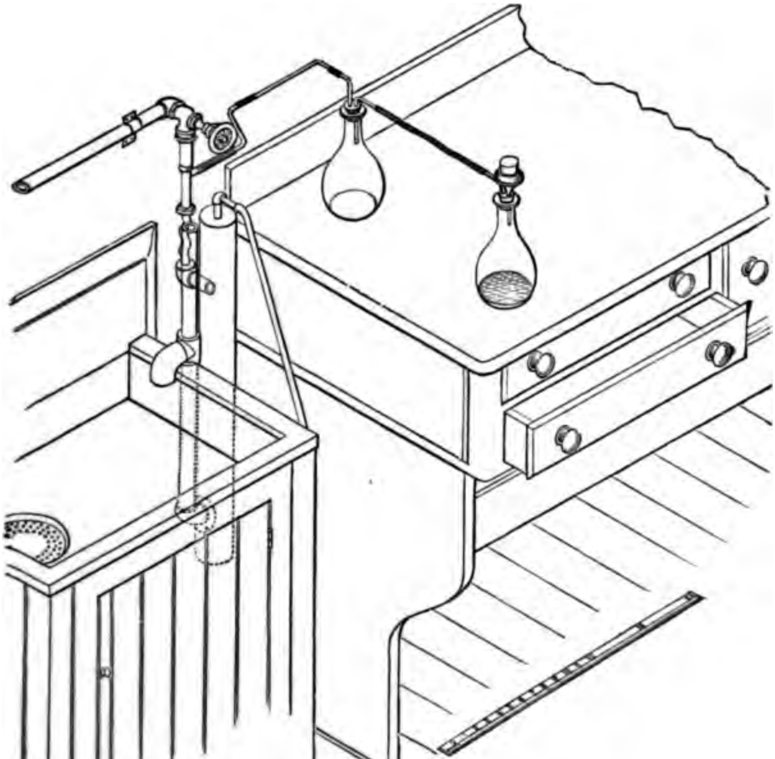


Filter-Pumps.

The use of filter-pumps for Bunsen's method of rapid filtration is now very general, and greatly facilitates many operations. The kind of pump is usually determined by the water-supply. With a good pressure of water, the most convenient form of pump is the injector. Fig. 17 shows the Richards injector united with an air-cylinder, from which a current of air sufficient for an ordinary blast-lamp may be obtained. When the pump is used for filtering strong solutions of nitric acid a glass injector may be used, and the water allowed to flow at once into the sink or waste-pipe. When the pressure of water is not great enough for an injector the Bunsen pump may be used, the vacuum obtained of course depending on the amount of fall. A tank with a ball-cock attachment makes this form of pump most convenient.

An ordinary air-pump may also be used for many purposes, but of course is unsuitable for filtering corrosive liquids, such as nitric acid, unless a wash-bottle containing a caustic alkali is interposed between the flask and the air-pump. The apparatus shown in Fig. 18 will give a very good idea of an arrangement which is very convenient when a water-supply is not available. The jug, which may be of three or five gallons' capacity, serves as a reservoir. It connects directly with the air-pump.

FIG. 17.



Bunsen's Method of Rapid Filtration.

This method is too widely known to make a detailed description necessary, but some hints in regard to the details may be useful. In the first place, it is very difficult to get good 60° funnels, so that the little perforated cones of platinum to support the point of the filter, which are sold by chemical dealers, rarely fit the funnel, and when they do not fit, the filters are apt to tear. The small funnel of platinum foil, as recommended by Bunsen, can be made to fit the funnel better, but the edges sometimes cut the filter. A small funnel of parchment pricked full of pin-holes, and of the size and shape of the platinum-foil funnel, works very well. It is a mistake to use too great a pressure, especially at first, and the filter should be kept full. The filtering-flask should always be connected, not with the vacuum-pipe directly, but with another flask fitted with a little Bunsen valve, which allows the air to pass into the vacuum-pipe, but, in case of a sudden stoppage in the pump, prevents the back pressure from entering the filtering-flask and blowing out the contents of the funnel.

FIG. 18.

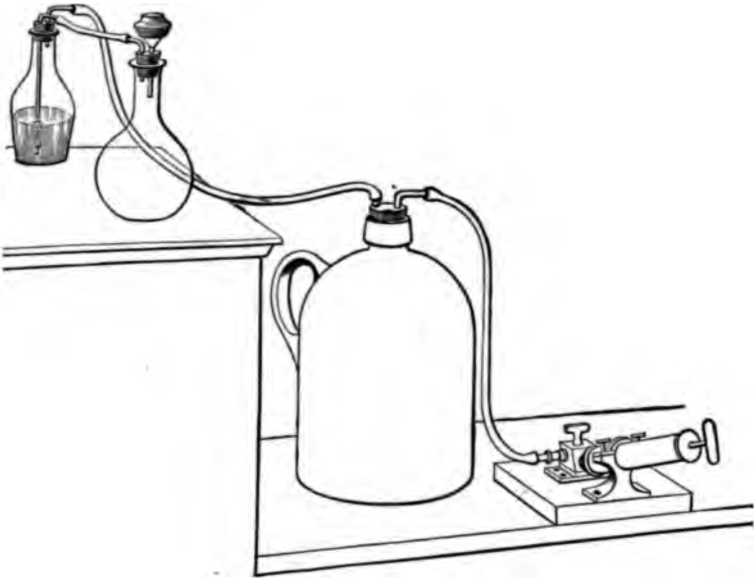


FIG. 19.

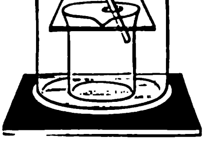


Fig. 19 shows an arrangement for filtering into a beaker instead of into a flask. It is necessary to have a glass cover over the beaker, as shown in the sketch, on account of the tendency the solution has to spatter, particles of the solution being carried out of the beaker in the current of air flowing into the vacuum-pipe.

Gooch's Method of Rapid Filtration.

The pierced crucible and cone, with asbestos felt, devised by Gooch,* are almost indispensable to the iron analyst for the proper and rapid execution of many operations, as will be seen by the frequent references to them in the descriptions of the methods given farther on. Fig. 20 shows the crucible and cap, and Fig. 21 the cone. The asbestos, which should be of a soft, silky, flexible fibre, is scraped longitudinally (not cut) to a fine, soft down, purified by boiling in strong hydrochloric acid, and washed thoroughly on the cone. It may be dried and kept in a bottle. The perforated crucible is placed in one end of a piece of soft rubber tubing, the other end of which is stretched over the top of a funnel, as shown in Figs. 20 and 22. The neck of the funnel passes through the stopper of a vacuum-flask. To prepare the felt, pour a little of the prepared asbestos suspended in water into the crucible and attach the pump. The asbestos at once assumes the condition of a firm, compact layer, which is washed with ease under the pressure of the pump. After washing the felt, suck it dry on the pump, remove the crucible, detach any little pieces of fibre that may be on the outside of the bottom of the crucible, slip on the little cap, dry, ignite, and weigh. Remove the cap, place the crucible in the rubber holder, start the pump, and pour the liquid and precipitate to be filtered into the crucible, wash, dry, ignite, if required, cool, and

FIG. 20.

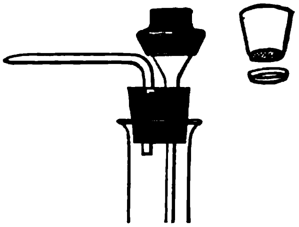


FIG. 21.

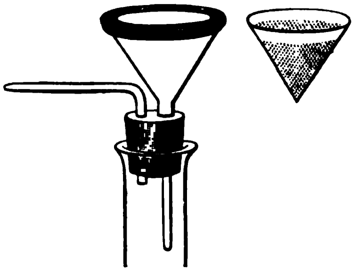
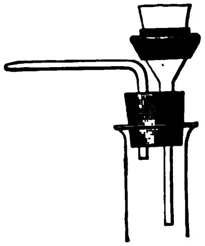


FIG. 22.



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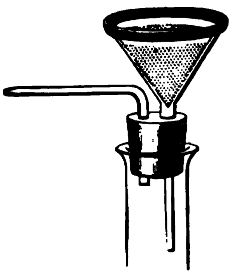
* Proceedings Am. Acad. Arts and Sciences, 1878, p. 342; Chem. News, xxxvii. 181.

weigh as before. The cone is fitted to a funnel by means of a rubber band stretched over the top of the funnel. The pressure of the pump pulls the cone down so that the overlapping part of the band forms a tight joint between the cone and the upper part of the funnel (Fig. 23). The felt is prepared in the same manner as in the crucible. Fill the cone with the asbestos suspended in water, start the pump, press down the cone into the funnel, and, if necessary, pour in more of the asbestos, letting it run all around from the upper edge of the cone so as to fill all the holes and make a firm, cohesive layer all over the inside of the perforated portion of the cone. Wash it well with water and suck it dry. It will then be ready for use. The cone is not intended for use when the precipitate is to be weighed, but, as it presents a very large filtering surface, it is most useful for such precipitates as manganese dioxide precipitated by Ford's method, etc. In this case, when the precipitate has been washed and sucked dry, by removing the cone from the funnel and carefully separating the felt from the sides of the cone with a little piece of flattened platinum wire, it may be removed from the cone with the precipitate enclosed in it, and the whole mass transferred to a beaker or flask for resolution. The cones may be of various sizes; for ordinary use, a cone 1¾ inches (45 mm.) in diameter is very convenient. They may also be used with a paper filter. In both the crucibles and cones the holes should be very small, and drilled (not punched) as closely together as possible.

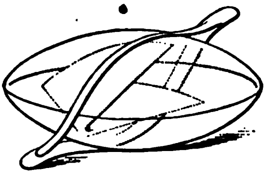
FIG. 23.



Counterpoised Filters.

The Gooch crucible and felt are most useful for weighing precipitates which are to be dried and not ignited, as in the direct weighing of the phospho-molybdate of ammonium. When they are not available, however, recourse must be had to counterpoised filters. The best method for preparing and using them is as follows. Take two washed filters of the same size and about the same thickness, fold them as if about to fit them in funnels, and, by cutting from the upper edge of the heavier of the two with a pair of scissors, make them nearly balance. Place them between a pair of watch-glasses, as shown in Fig. 24, dry them at 100° C., and allow them to cool in a desiccator. Place one in each pan of the balance, and, handling them with a pair of forceps, clip them until they balance exactly. Place each filter in a funnel, filter the precipitate on one of them, pass the *clear* filtrate (not the washings) through the other, and wash them both in the same manner. Remove them from the funnels, turning over the top edges of the filter containing the precipitate to prevent any of the latter from falling out, place them in a watch-glass, dry them at 100° C. (or at the required temperature, whatever it may be), cover them with the other watch-glass, cool in a desiccator, place them on opposite pans of the balance, and the weight added to the pan containing the empty filter, to make them balance, is the weight of the precipitate.

FIG. 24.



Filter-Paper.

All filter-paper contains more or less inorganic matter, which remains, after burning the paper, as a white or brownish ash. The Swedish paper with the water-mark J. H. Munktell leaves the smallest amount of ash, and this ash contains from 35 to 65 per cent. silica, besides ferric oxide, alumina, lime, and magnesia in varying proportions.

Schleicher & Schull and Baker & Adamson prepare very pure filters by washing them with hydrochloric acid and hydrofluoric acid, and these should always be used for very accurate work. The commoner kinds of German paper contain much larger amounts of inorganic matter than the Swedish paper, which consists principally of calcium carbonate, but sometimes contains appreciable amounts of phosphates.

Washing-Bottles.

Figs. 25, 26, 27, and 28 represent different forms of washing-bottles. Fig. 25 shows a bottle for use with ether or acids. The stopper is of glass. For ordinary use that represented in Fig. 26 is the best. The neck is wrapped with thin asbestos board, covered with a piece of wash-leather or chamois, which is sewed to keep it from slipping. This is very necessary when hot water is used. A piece of soft rubber tubing at A is more pleasant for the mouth than the glass, and after compressing the air in the flask the tube can be grasped with the teeth, thus keeping up the stream of water for some time without effort. It also prevents the lips from being scalded when using very hot water. Fig. 27 shows a movable tip, which allows the stream of water to be directed by means of the finger. The form of flask shown in Fig. 27 is very convenient to use with ammonia-water, etc. The tube *a* is closed with the index finger, while the Bunsen valve *b* closing as soon as the air is compressed in the flask prevents the vapors from coming back into the mouth, and the stream of liquid is stopped instantly by removing the finger from *a*. Fig. 28 shows the Berzelius form, which is sometimes very useful. The air is compressed by blowing into the bottle through the jet, and by quickly inverting the bottle the stream of liquid is forced out until the equilibrium is restored. It requires a little practice to use this form of bottle easily, but when the art is once acquired it can be used with ammonia-water as well as pure water, and the facility with which it can be removed and pointed in any direction with the hand makes it most convenient for some purposes.

FIG. 25.

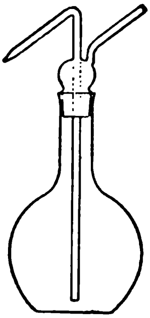


FIG. 26.

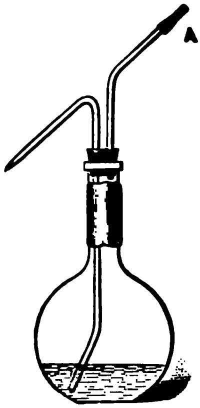


FIG. 27.

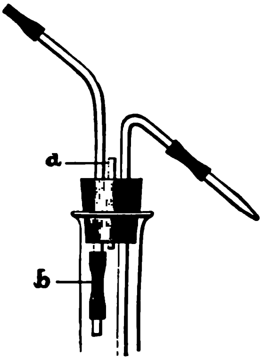
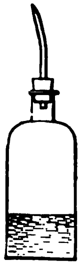


FIG. 28.



Removing Precipitates from Beakers.

A feather trimmed in the way shown in Fig. 29 may be used to remove particles of adhering precipitates from beakers, evaporating-dishes, etc.

A piece of soft rubber tubing on the end of a piece of glass rod or sealed glass tube is much more effective and convenient in most cases. It is made by taking a short length of rubber tubing, placing a little pure caoutchouc dissolved in chloroform or naphtha in one end, squeezing the sides together between two pieces of board (Fig. 31), and allowing it to remain for at least twenty-four hours. It may then be trimmed down and placed on the end of a piece of glass rod or on the end of a piece of glass tubing having the ends fused together (Fig. 30). This little instrument has acquired the name of "policeman."

FIG. 29.

FIG. 30.

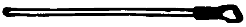
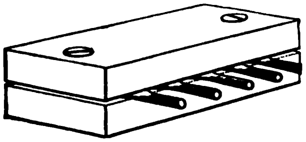


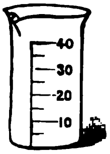
FIG. 31.



Measuring-Glasses.

In adding reagents to a sample or to a solution, measured amounts should nearly always be used, and, as it is generally well under all circumstances to avoid adding them from the bottle direct, little beakers of the form shown in Fig. 32 are very useful. They can be graduated and marked by covering the side with a thin coating of paraffine, measuring in water from a burette, marking the levels and amounts in the paraffine with a sharp-pointed instrument, and etching them in the glass by filling the marks with hydrofluoric acid. After standing a few minutes the hydrofluoric acid may be washed off under the hydrant and the paraffine removed with hot water. As the amounts are intended to be only approximate, no great degree of care need be exercised in the graduation.

FIG. 32.



Caps for Reagent-Bottles.

The stoppers and lips of reagent-bottles are very apt to become covered with ammonium chloride, dust, etc., when exposed in the laboratory, and especially such as are not in constant use,—volumetric solutions, stock-bottles, etc. It is well to keep them always covered with caps, which may be bought from the dealers, or with cracked beakers, which answer the purpose nearly as well in most cases.

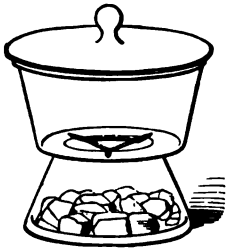
Rubber Stoppers.

Rubber stoppers are now generally used instead of cork. Solid stoppers should always be purchased, and the holes cut with the ordinary cork-borers. This is readily done by moistening the cork-borer with water or alcohol. A little practice will enable any one to do this with great ease.

Desiccators.

Crucibles should always be cooled before weighing in desiccators. The form shown in Fig. 33 is most convenient. The desiccator should contain fused calcium chloride. The crucible rests on a small triangle, which may be made of copper wire, each side being covered by winding a thin strip of platinum foil around it to prevent the crucible from coming in contact with the copper, which may become more or less corroded.

FIG. 33.

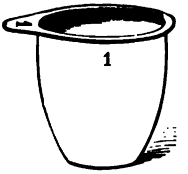


PLATINUM APPARATUS.

Crucibles.

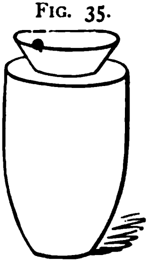
The shape of the crucible is of considerable importance as regards its wearing properties. Fig. 34 shows the best form for general use. A crucible $1\frac{1}{2}$ inches (38 mm.) high, $1\frac{5}{16}$ inches ($33\frac{1}{2}$ mm.) wide at the top, with a capacity of 20 c.c., and weighing with the lid about 25 grammes, is well adapted for weighing the usual precipitates found in the course of iron analysis. For fusions a much larger crucible is necessary: one $1\frac{13}{16}$ inches (46 mm.) high, $1\frac{13}{16}$ inches (46 mm.) wide on top, with a capacity of 55 c.c., and weighing about 60 grammes, will be found convenient and serviceable. Pure platinum is the best metal for crucibles. The iridium alloy, at one

FIG. 34.



time so popular, has not been found to wear well. It is stiffer than the pure metal, but much more liable to crack. The endurance of a crucible depends very much upon the treatment it receives. The salts of easily reduced metals fusing at a low temperature, such as lead, tin, bismuth, antimony, etc., should never be ignited in platinum; besides these, the phosphoric acid in some phosphates is occasionally partly reduced, rendering the platinum very brittle. A platinum crucible should never be bent out of shape when it can be avoided, and a wooden plug exactly the shape of the crucible (Fig. 35) is very useful to straighten it on when it has been bent. It should always be carefully cleaned before use: the precipitate last ignited should be dissolved in acid if possible, and the crucible washed out with water, dried, ignited, and cooled in a desiccator before weighing. A precipitate of ferric oxide will sometimes stain a crucible very badly; this stain may be removed by allowing the crucible to stand with cold hydrochloric acid for twelve hours, and then warming it for a short time. Stains that are not removed by hydrochloric acid may be removed by fusing potassium bisulphate in the crucible, or by fusing sodium carbonate in it, dissolving in water, and then treating the crucible with hydrochloric acid. Whenever a crucible begins to look dull and tarnished it should be cleaned inside and out with very fine sea-sand (not sharp sand) by moistening the finger, dipping it in the sand, and rubbing the crucible with it. This method of cleaning decreases the weight of the crucible very slightly, the sea-sand burnishing without cutting the crucible. It is very convenient to have each crucible and its cover marked with a number, as shown in Fig. 34.

FIG. 35.



Dishes.

Fig. 36 shows a very convenient form of dish for the determination of **silicon in pig-iron, silica in iron ores, etc.** It is $3\frac{1}{4}$ inches (83 mm.) in **diameter and $2\frac{1}{4}$** inches (57 mm.) high. Fig. 37 is for such work as precipi-**tation of ferric oxide, etc.** It is 5 inches (127 mm.) in diameter and $3\frac{5}{16}$ **inches (84 mm.) high.** The wire which is fused into the top of the dish makes it much stiffer than it would otherwise be, and consequently it may be made lighter and cheaper than would be possible without the wire. The wire is hammered out and helps to form the lip. A platinum stirring-rod, formed from a piece of seamless tubing, rounded and fused together at the ends, is useful for many purposes. It may be from 5½ to 7 inches (140 to 179 mm.) long, ¼ inch (6 mm.) in diameter, weighing from 7.5 to 11 grammes.

FIG. 36.

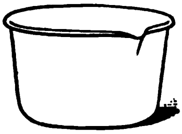
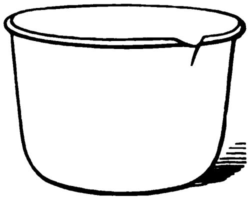


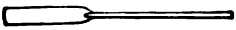
FIG. 37.



Spatula.

Fig. 38 shows a very convenient and useful form of spatula. The blade which is made of the platinum-iridium alloy, is fused into a tube of the same alloy which forms the handle. The weight of the spatula in the sketch is 14 grammes, length 6½ inches (165 mm.).

FIG. 38.



Triangles and Tripods.

The triangles for supporting the crucibles during the ignition are shown in Figs. 12 and 13, as are also tripods for holding the lids, etc. These are made from wire about $\frac{1}{16}$ inch (1.6 mm.) diameter, the ends are fused, and the wire, where it is twisted, has the parts in contact fused together almost to the inside of the triangle, which makes it much stiffer. The triangles should be attached to the iron rings of the supports with a few turns of fine platinum wire.

Crucible-Tongs.

Fig. 39 shows the best form of crucible-tongs. The part from *a* to *b* is of platinum, the straight part from *a* to *c* fitting over the end of the iron. The surfaces at *d* are in contact when the tongs are closed, and with this portion the lid can be handled, and the crucible is clasped by the curved ends, which hold it firmly without danger of bending the crucible. They are especially useful in handling a crucible containing a liquid fusion. Another form, shown in Fig. 40, is generally of brass, the points and bend being lined with platinum. A small pair of forceps (Fig. 41) is useful for taking the crucible from the desiccator and placing it on the balance, the lid of the crucible being slipped a little to one side to allow one of the points of the forceps to go inside the crucible.

FIG. 39.

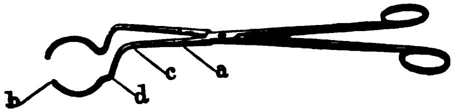


FIG. 40.

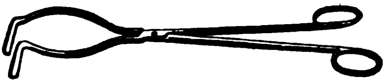
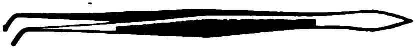


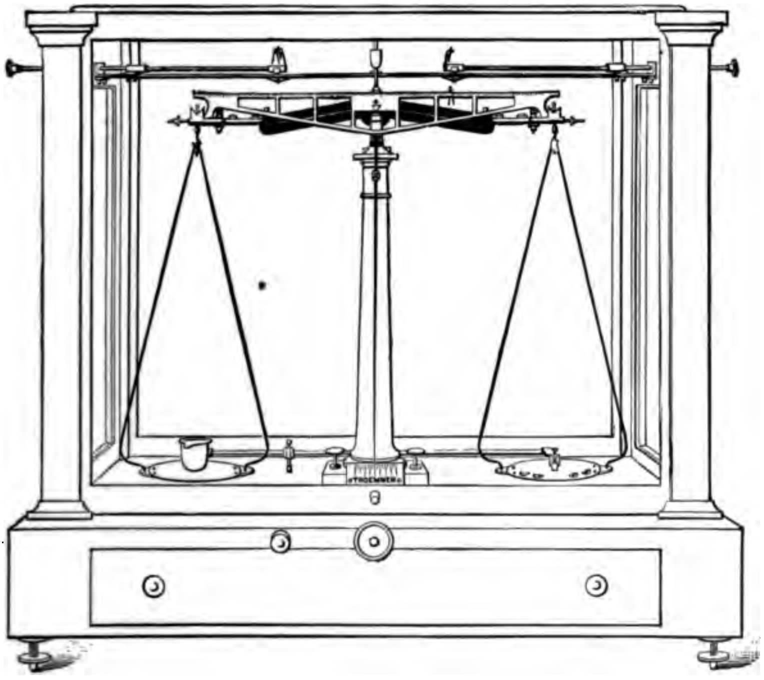
FIG. 41.



Balances.

The balance is one of the most important things in the equipment of a laboratory, and a cheap balance is nearly always a very poor investment. The quality of balances has improved greatly in the last few years, and it is now possible to get a most admirable instrument of this kind at a com-

FIG. 42.



paratively low price. Fig. 42 shows a balance which for sensitiveness and quickness is unsurpassed. It is made to carry up to 200 grammes in each pan. The beam is of aluminum, as are also the pans. The stirrups are of nickel, the knife-edges and bearings of agate, while the arrangement for carrying the riders (Fig. 43) is most ingenious and effective. It is of course very convenient to have one balance for weighing crucibles, etc., and another for weighing samples for analysis. The balance for the latter purpose may be much smaller than the balance for the former, and should be provided with a small aluminum pan with a spout (Fig. 44), to facilitate the transfer of samples to flasks, test-tubes, etc. The pan should have a counterpoise. A pair of small forceps, slightly magnetized, may be used to advantage in getting exact weights of steel drillings, and a camel's-hair brush is necessary to detach small particles of ore, etc., from the aluminum pan or balanced watch-glasses.

FIG. 43.

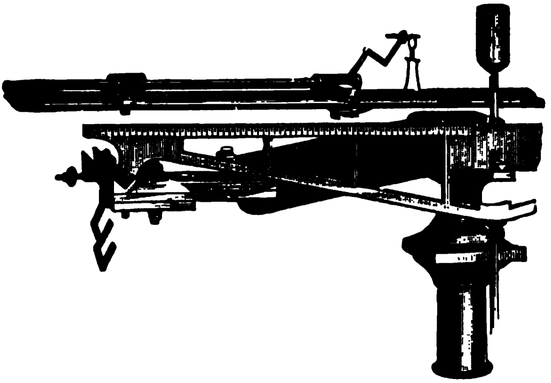
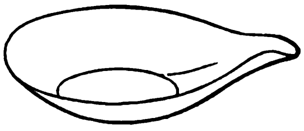


FIG. 44.



Factor Weights.

The use of factor weights is in many cases extremely convenient, as it does away with all calculation, and is to that extent time-saving and valuable in avoiding one source of error. Thus, in determining carbon by combustion in steel, using 2.7273 grammes of the steel, 0.1 milligramme of carbonic acid is equal to 0.001 per cent. of carbon in the steel. For determining silicon in pig-iron the ¼ factor weight, or 1.1755 grammes, is very

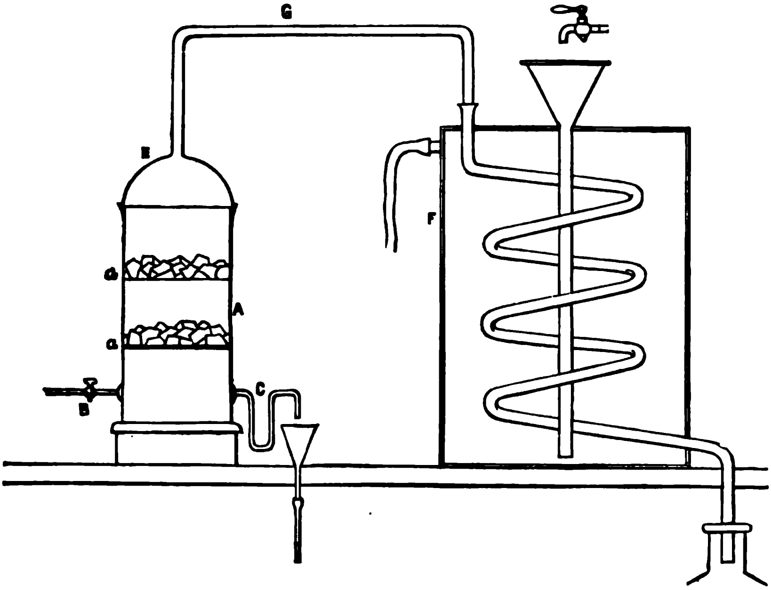
convenient. When the weight of silica is multiplied by 4, one milligramme is equal to 0.01 per cent. of silicon. Or, for rapid silicon determinations, **the** $\frac{1}{10}$ factor weight, 0.4702 gramme, is used.

REAGENTS.

Distilled Water.

When only a small amount of distilled water is needed, a tin-lined copper still and condenser, such as are furnished by all dealers, may be used, but where there is a supply of steam, an arrangement like that shown in Fig. 45 will be found most useful. A is a tin-lined copper cylinder, with a dome-shaped top, E, fitted to A by the joint shown in the sketch, which may be made tight by paper or a linen rag. Two perforated shelves, *a*, *a*, support layers of clean quartz-gravel or pieces of block-tin, which wash the

Fig. 45.



steam and prevent dirt from being carried over mechanically. The steam enters at B, and the water condensed in the cylinder A passes off through the pipe C. The washed steam passes up through the block-tin pipe G, and is condensed in the worm-tub F. A glass worm should never be used, as the water condensed in it dissolves notable amounts of glass.

ACIDS AND HALOGENS.

Hydrochloric Acid. HCl. Sp. gr. 1.2.

Chemically pure hydrochloric acid is readily obtained. It should be free from chlorine, sulphuric and sulphurous acids, arsenic, and fixed salts. To test for sulphuric and sulphurous acids, evaporate 100 c.c. to dryness with a little pure potassium nitrate, redissolve in water with a few drops of hydrochloric acid, filter, if necessary, and add barium chloride. To test for arsenic, put into a clean dry test-tube a few centigrammes of pure stannous chloride, pour in carefully 6 or 8 c.c. hydrochloric acid, and gradually 2 or 3 c.c. pure sulphuric acid, shaking the test-tube gently. If the hydrochloric acid is free from arsenic the solution remains clear and colorless, but if arsenic is present the solution becomes yellowish, then brownish, and finally metallic arsenic is deposited. The test-tube should be gently warmed if no reaction occurs at first. To test for chlorine, pour some of the acid into a solution of potassium iodide containing a little starch solution. A blue coloration indicates chlorine or ferric chloride. To test for metallic salts, neutralize about 100 c.c. of the acid with ammonia and add ammonium sulphide. To test for salts of the alkalies, evaporate about 100 c.c. of the acid to dryness, and test any residue which may remain.

Nitric Acid. HNO_3. Sp. gr. 1.41.

Nitric acid should be free from nitrous acid, the presence of which may be known by the yellowish color it produces. It may be freed from this gas by passing a current of air through the acid until it becomes colorless. To test for hydrochloric acid or chlorine, dilute largely and add a solution of silver nitrate. To test for fixed salts, evaporate about 100 c.c. to dryness. The ordinary acid diluted with an equal volume of water gives the acid of 1.2 sp. gr. used to dissolve steel for the color carbon test. It should be carefully tested for chlorine and hydrochloric acid.

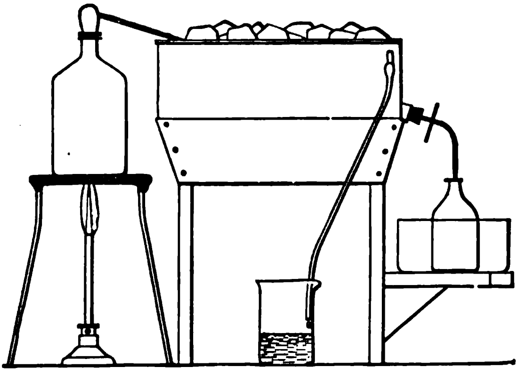
Sulphuric Acid. H_2SO_4. Sp. gr. 1.84.

Sulphuric acid should be colorless. To test for oxides of nitrogen, Warington * suggests placing about two pounds of the acid in a bottle, which it half fills, and shaking violently. The air washes the gases out of the acid, and the presence of the oxides of nitrogen may be detected by placing in the mouth of the bottle a piece of filter-paper saturated with potassium iodide and starch solution, which is colored blue when any of these oxides are present. To test for lead, supersaturate some of the acid with ammonia and add ammonium sulphide.

Hydrofluoric Acid. HFl.

The use of ceresine bottles, suggested by Prof. Edward Hart, of Lafayette College, has made it quite possible to obtain pure hydrofluoric acid, but the crude acid may be redistilled into platinum bottles in the laboratory. The crude acid, which may be purchased from glass engravers and etchers, is distilled from a platinum, silver, or lead still, as shown in Fig. 46. The head of the still and condensing-tube is of platinum. The condensing tube runs through a copper box filled with ice, and a platinum bottle receives the condensed acid. Where the tube comes through the lower part of the box it is secured by a rubber stopper, and a small bit of paper around the tube prevents any

FIG. 46.



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* Crookes's Select Methods, 2d ed., p. 494.

condensed moisture on the outside of the tube from running into the bottle. Before distilling the acid, put into it a few crystals of potassium permanganate and a few c.c. of sulphuric acid. The redistilled acid should leave no residue upon evaporation.

Acetic Acid. $H,C_2H_3O_2 + Aq$. Sp. gr. 1.04.

Acetic acid of the strength given above is the best for use in iron analysis. It should give no residue on evaporation, and no precipitate upon neutralization with ammonia and the addition of ammonium sulphide. It should be free from phosphoric acid. To test it for phosphoric acid, evaporate 100 c.c. nearly to dryness, add a little magnesium mixture and a large excess of ammonia, cool in ice-water, and stir vigorously. When phosphoric acid is present, a precipitate of ammonium magnesium phosphate will be obtained.

Citric Acid. $H_3,C_6H_5O_7,H_2O$.

Citric acid is easily obtained in a state of purity in the form of crystals having the above composition. It should be kept in the solid condition, and dissolved as needed. It is soluble in ¾ part of water at 15° C.

Tartaric Acid. $H_2,C_4H_4O_6$.

Tartaric acid is also easily obtained sufficiently pure for use in iron analysis. The crystals should be dissolved only as needed. The only impurity is a small amount of lime. It is soluble in ½ part of water at 15° C.

Oxalic Acid. H_2,C_2O_4.

Oxalic acid crystallizes from its aqueous solution as $H_2,C_2O_4,2H_2O$, soluble in 8.7 parts of water at 15° C. It loses its water of hydration very easily even at the ordinary temperature in dry air, and very quickly at 100° C.

Bromine. Br.

Bromine is easily obtained in a condition sufficiently pure for use as a reagent. It is a dark brown, extremely corrosive liquid, of sp. gr. 2.97.

It is soluble in about 30 parts of water at 15° C. It is best kept in a glass-stoppered bottle with a ground cap. As the aqueous solution is generally used, it is convenient to put only a small amount—say 20 or 30 c.c.—in the bottle, fill the bottle nearly full of cold distilled water, shake it up well, and pour off the saturated solution as required. There usually remains in the bottom of the bottle a small amount of impurity, which is insoluble in water.

Iodine. I.

Iodine is a metallic-looking crystalline solid, of sp. gr. 4.95. Resublimed iodine is not sufficiently pure for use, and must be redistilled with great care, unless it is used as iodine dissolved in iodide of iron, and filtered. To distil it, place about ½ kilo. in a large glass retort of about 2 litres' capacity connected with an adapter about 18 inches (456 mm.) long and 3 inches (75 mm.) in diameter at the largest part. The heat from a Bunsen burner turned quite low will cause the violet vapors of iodine to pass rapidly into the adapter, where they will condense without any means being taken to cool it. By gently warming the outside of the adapter after the distillation has been finished, the iodine may readily be detached in large masses and removed. It should be kept in a wide-mouth, glass-stoppered bottle.

Chlorine. Cl.

Chlorine is a yellowish gas about two and one-half times heavier than air. It is sparingly soluble in water. When required it must be made. The details are given under "Determination of Silicon in Iron and Steel."

Sulphurous Acid. H_2SO_3.

To make sulphurous acid gas, mix powdered charcoal and strong sulphuric acid until a thin paste is formed, heat the paste in a flask, very gently at first, and pass the gas through a washing-bottle containing a little water. The reaction is $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$. The tube leading from the flask into the washing-bottle should have a bulb in it to prevent the reflux of water into the flask in case of sudden cooling. Clippings of sheet copper, or copper turnings, may be used instead of charcoal, and are generally to be preferred. The best proportion is 250 grammes of copper to 500 c.c. of strong sulphuric acid. The aqueous solution of the gas is made by passing the washed gas into distilled water.

A very neat and inexpensive method of making saturated solutions of sulphurous acid is to buy the small cylinders containing about 20 ounces of liquefied gas each. One of these cylinders contains enough gas to saturate ten litres of water. They are closed with a small lead tube fused at the end. Straighten out the tube as far as possible, cut off the fused end and slip a piece of rubber tubing, connected with a washing-bottle, over it and allow the gas to flow through. The gas, SO_2, has a specific gravity of 2.21 (air = 1). 1 c.c. of water at 15° C. dissolves 0.1353 gramme of SO_2.

Chromic Acid. CrO_3.

Chromic anhydride as a red powder or in the form of scarlet crystals is easily obtained in a state of purity. It is deliquescent, and dissolves in a small quantity of water, forming a dark brownish-colored liquid. It may be made by pouring 1 volume of a saturated solution of potassium bichromate into 1½ volumes of strong sulphuric acid, stirring constantly. The liquid on cooling deposits needles of chromic anhydride, which must be separated from the mother-liquid and purified by recrystallization.

GASES.

Carbon Dioxide. Carbonic Acid Gas. CO_2.

The best form of generator is shown in Fig. 47. It was first suggested by Casamajor.* It consists of a large tubulated bottle, the bottom of which is covered to the depth of about 1 inch (25 mm.) with buckshot, on top of which rest lumps of marble. Dilute hydrochloric acid (1 acid to 5 water) is admitted through the tube which enters at the tubulure at the bottom of the bottle, bending down so as to reach the bottom of the bottle. The wash-bottle A contains water. By blowing in the rubber tube attached to the acid-bottle the acid passes over into the tubulated bottle. When the stopcock K is closed, the pressure in the tubulated bottle forces the acid back into the acid-bottle. When the acid becomes exhausted and remains in the tubulated bottle, pour a little strong hydrochloric acid into the acid-bottle and blow it over into the tubulated bottle. The generated gas will force the liquid back into the acid-bottle, when it can be replaced by fresh acid. A slightly different form is shown in Fig. 50.

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* American Chemist, vi. 209.

Hydrogen Sulphide Gas. H_2S.

The same form of apparatus is used for generating hydrogen sulphide. Ferrous sulphide is substituted for marble, but hydrochloric acid is used instead of sulphuric acid, as is generally advised, for the ferrous sulphate formed crystallizes out and clogs the apparatus.

Hydrogen. H.

The same form of apparatus as that used for carbonic acid and hydrogen sulphide can be used to advantage for generating hydrogen gas. Pieces of zinc, which may be obtained by melting the zinc and pouring it in a sheet about ¼ inch (6 mm.) thick, so that it can easily be broken, are to be used, and not granulated zinc. Hydrochloric acid is better than sulphuric.

Oxygen Gas. O.

Oxygen compressed in cylinders can be obtained from most dealers in chemicals, but it should always be carefully tested before being used for the determination of carbon in steel or iron, as the cylinders are sometimes filled with coal-gas, and a cylinder which has once held coal-gas is rarely free from hydrocarbons.

The gas may be made on a small scale in the laboratory by carefully mixing in a porcelain mortar 100 grammes potassium chlorate and 5 grammes powdered manganese dioxide, transferring to a retort, which the mixture should not more than half fill, and heating carefully over a Bunsen burner. The evolved gas may be collected in a gas-holder or in an india-rubber bag. The latter is not to be recommended for use for carbon determinations, as rubber is very liable to give off hydrocarbons.

ALKALIES AND ALKALINE SALTS.

Ammonium Hydroxide. Ammonia. NH_4HO.

The solution of ammonia gas (NH_3) commonly used is of sp. gr. 0.88, and contains about 30 to 35 per cent. of ammonia. It should be kept in glass-stoppered bottles and in a cool place, as the gas passes off very rapidly even at the ordinary temperature when open to the air. It should be colorless, leave no residue upon evaporation, be free from chlorides and sulphates, and give no precipitate with hydrogen sulphide.

Ammonium Bisulphite. NH_4HSO_3.

Ammonium bisulphite is made by passing sulphurous acid gas into strong ammonia until the solution becomes yellowish in color and smells strongly of sulphurous acid. By the first method of manufacture of sulphurous acid given on page 41, a large amount of carbonic acid is formed at the same time, which is absorbed by the ammonia. This is gradually displaced by the sulphurous acid, and, if the solution is kept cool, white crystals of the neutral sulphite, $(NH_4)_2SO_3H_2O$, are deposited. These are gradually dissolved by the excess of sulphurous acid until the solution becomes quite clear, assuming a yellowish tint. When copper is used instead of charcoal, no carbonic acid is evolved and no ammonium carbonate is formed. The cylinders of liquefied gas mentioned on page 42 may be used for this purpose. One cylinder will saturate about one litre of strong ammonia. By exposure to air ammonium bisulphite is gradually oxidized to sulphate. Old ammonium bisulphite always contains a small amount of hyposulphite, which occasions a precipitate of sulphur when deoxidizing solutions of ferric salts. It is not now difficult to purchase pure ammonium bisulphite, but sodium bisulphite is very apt to contain phosphoric acid. When made from strong ammonia-water, 18 c.c. of bisulphite will deoxidize a solution of 10 grammes of iron or steel.

Ammonium Sulphydrate. Ammonium Sulphide. $(NH_4)_2S$.

Ammonium sulphide is made by saturating strong ammonia with hydrogen sulphide and adding an equal volume of ammonia. The reactions are

$$NH_4HO + H_2S = NH_4HS + H_2O \text{ and}$$
$$NH_4HS + NH_4HO = (NH_4)_2S + H_2O.$$

The solution becomes yellow by age or by exposure to the air.

Ammonium Chloride. NH_4Cl.

Ammonium chloride is a white, crystalline, anhydrous salt, soluble in about its own weight of water at 100° C., and in 2.7 parts of water at 18° C. It volatilizes when heated without previous fusion. The salt is usually purified by sublimation. It generally contains a little iron, but is free from other impurities. To prepare ammonium chloride for use in J. Lawrence Smith's method for decomposition of silicates, dissolve it in boiling water and evaporate down on a water-bath or air-bath. When the salt begins to crystallize out, stir vigorously. The crystals formed will be very small. Drain off the liquid and dry. The salt can then readily be powdered.

Ammonium Nitrate. NH_4NO_3.

Ammonium nitrate is a white, crystalline salt, soluble in one-half its weight of water at 18° C., and in much less at 100° C. When dissolved in water it produces great cold. By evaporation it loses ammonia and becomes acid. When heated it fuses at 108° C., and is decomposed between 230° C. and 250° C. into water and nitrous oxide, $NH_4NO_3 = 2H_2O + N_2O$. It should leave no residue when volatilized.

Ammonium Fluoride. NH_4Fl.

Ammonium fluoride may be made by saturating hydrofluoric acid by ammonia. The salt crystallizes when left to evaporate over quicklime. It is slightly deliquescent, and therefore difficult to keep, as the solution attacks glass.

Ammonium Acetate. $NH_4C_2H_3O_2$.

Ammonium acetate is best made by slightly acidulating ammonia by acetic acid. One volume of strong ammonia-water requires about 2 volumes of acetic acid, 1.04 sp. gr., to neutralize it. It is best to make it as needed, as it decomposes when kept.

Ammonium Oxalate. $(NH_4)_2C_2O_4 + H_2O$.

Ammonium oxalate is a white salt, crystallizing in long prisms united in tufts. It is soluble in 20 parts of water at 18° C.

Sodium Hydroxide. Caustic Soda. $NaHO$.

Fused sodium hydroxide purified by alcohol is sufficiently pure for ordinary purposes. It forms white opaque masses, having a strong affinity for water. It dissolves in water with evolution of heat. Pure sodium hydroxide is prepared by allowing metallic sodium to decompose water in a platinum dish. It must be kept in a silver or platinum bottle, as the solution acts very rapidly on glass.

Sodium-Ammonium Phosphate. Microcosmic Salt. $NaNH_4HPO_4,4H_2O$.

Sodium-ammonium phosphate (microcosmic salt) is a white, crystalline salt, soluble in 6 parts of cold and 1 part of hot water. It should not be kept in solution for any great length of time, as it attacks glass very readily. It loses its water of crystallization very easily, and when heated gives off its ammonia, leaving pure sodium metaphosphate, which in the fused condition dissolves metallic oxides in many cases with the production of characteristic colors, which makes it a valuable reagent for blow-pipe analysis. It is easily obtained in a state of purity.

Sodium Carbonate. Na_2CO_3.

Sodium carbonate is never quite pure. It always contains small amounts of silica, alumina, lime, and magnesia, besides sulphuric acid. It may generally be obtained quite free from phosphoric acid. Every lot should be carefully examined for all the above impurities, and the amount per gramme noted, so that the proper subtraction may be made in each analysis. It is used in solution only for the neutralization of solutions, as in the determination of manganese by the acetate method, and, as the solution attacks glass very rapidly, it is best to dissolve the salt only as it is needed.

Sodium Nitrate. $NaNO_3$.

Sodium nitrate is used occasionally instead of potassium nitrate in making fusions of ores containing titanic acid. It may be prepared by acidulating a strong solution of sodium carbonate with nitric acid, heating until the water and excess of nitric acid are driven off, and powdering the dry salt.

Sodium Hyposulphite. Sodium Thiosulphate. $Na_2S_2O_3 + 5H_2O$.

Sodium hyposulphite is very soluble in water, but decomposes even in tightly stoppered bottles, sodium sulphate being formed and sulphur precipitated. It should, therefore, be dissolved only as used.

Sodium Acetate. $NaC_2H_3O_2 + 3H_2O$.

Crystallized sodium acetate dissolves in 3.9 parts of water at 6° C. It is rarely quite pure, containing, usually, calcium and iron salts, but it may be used after solution and filtration for partial analyses, as in the determination of manganese by the acetate method, etc. In complete analyses it is better to use ammonium acetate. When the use of sodium acetate is unavoidable, it can be made by dissolving C. P. sodium carbonate in acetic acid, boiling off the liberated carbonic acid, and adding acetic acid to slight acid reaction.

Potassium Hydroxide. Caustic Potash. KHO.

Potassium hydroxide purified by solution in alcohol, filtration, and subsequent evaporation to dryness and fusion, is quite pure enough for all the ordinary purposes of iron analysis. An aqueous solution of 1.27 sp. gr. is used to absorb carbonic acid in the determination of carbon in iron and steel, in the determination of carbonic acid in ores, etc. 300 grammes of fused potassium hydroxide dissolved in 1 litre of water will give a solution of about this strength.

Potassium Nitrite. KNO_2.

Potassium nitrite is used to separate nickel and cobalt. It is difficult to buy the pure salt, but it is easily made as follows. Heat 1 part of potassium nitrate in an iron dish until it is just fused, then add, with constant stirring, 2 parts of metallic lead. Raise the heat slightly to complete the oxidation of the lead, and allow the mass to cool. Treat the mass with water, filter from the lead oxide, pass carbon dioxide through the solution to precipitate the greater part of the dissolved lead oxide, and filter. To the filtrate add a little ammonium sulphide to precipitate the last traces of lead, filter, evaporate to dryness, and fuse in a platinum dish to decompose any hyposulphite that may have been formed, and preserve the fused salt for use. Potassium nitrite is deliquescent.

Potassium Nitrate. KNO_3.

Potassium nitrate is a white, crystalline salt, anhydrous, and soluble in 7½ parts of water at 0° C., and in 0.4 part of water at 100° C. It melts below a red heat to a colorless liquid, and at a red heat gives off oxygen gas more or less contaminated by nitrogen, being converted into potassium nitrite and potassium oxide. The salt may be purchased in a sufficient state of purity for all purposes of iron analysis, but, as it may contain small amounts of sulphuric acid, the amount should always be determined and the proper allowance made when it is to be used for the estimation of sulphur in ores.

Potassium Sulphide. K_2S.

Potassium sulphide is made by passing hydrogen sulphide into a solution of caustic potash and filtering from any precipitated alumina or ferrous sulphide. It is used instead of the corresponding ammonia-salt when the solution contains copper, as copper sulphide is slightly soluble in ammonium sulphide.

Potassium Bichromate. $K_2Cr_2O_7$.

Potassium bichromate is an orange-colored, anhydrous, crystalline salt, soluble in 20 parts of water at 0° C., and in 1 part of water at 100° C. It melts below a red heat to a transparent red liquid, crumbling to powder upon cooling. Heated with strong sulphuric acid it gives off about one-sixth its weight of oxygen gas, the reaction being $K_2Cr_2O_7 + 4H_2SO_4 = Cr_2K_2(SO_4)_4 + 4H_2O + 3O$. It is readily obtained in a state of purity, but should always be fused to destroy any organic matter before being used to determine carbon in iron or in ores.

Potassium Chlorate. $KClO_3$.

Potassium chlorate is a white, crystalline, anhydrous salt. It is soluble in about 30 parts of water at 0° C., and in about 2 parts at 100° C. It is readily decomposed by heat, first into a mixture of potassium chloride and perchlorate, a portion of the oxygen being set free, and at a higher temperature the perchlorate is decomposed, the remaining oxygen is given off and potassium chloride alone remains. It is easily obtained in a sufficient state of purity for use in iron analysis. Heated with nitric acid it yields potassium nitrate and perchlorate, water, chlorine, and oxygen, thus:

$$8KClO_3 + 6HNO_3 = 6KNO_3 + 2KClO_4 + 6Cl + 13O + 3H_2O.$$

Heated with hydrochloric acid it gives potassium chloride, water, and a mixture of chlorine peroxide and chlorine, called *euchlorine*, thus:

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + 9Cl.$$

Potassium Bisulphate. $KHSO_4$.

Potassium bisulphate is a white, crystalline salt, soluble in about one-half its weight of boiling water. A large amount of water decomposes it into potassium sulphate and free sulphuric acid; even in the presence of a large excess of sulphuric acid the neutral salt crystallizes out, leaving free sulphuric acid in the solution. Potassium bisulphate melts at 197° C.; at higher temperatures it gives off water, leaving the anhydrous salt, and at a red heat it gives off sulphuric acid, leaving the neutral sulphate. It is difficult to obtain it very pure, but it may be made as follows. Dissolve potassium bicarbonate in water, filter, and from a graduated vessel add sulphuric acid until, after boiling off the liberated carbonic acid, the solution is neutral, or but very faintly alkaline to test-paper. Filter, if necessary, and to the filtrate add as much sulphuric acid as was added in the first place to neutralize the bicarbonate. Boil the solution down, and finally fuse the mass in a platinum dish. Cool it, and when it is almost ready to solidify pour it into another dish. Break it up, and preserve it in glass-stoppered bottles.

Potassium Iodide. KI.

Potassium iodide is a white, crystalline, anhydrous salt, very soluble in water, and in dissolving it causes a fall of temperature in the solution. It is soluble in about 0.8 part of water at 0° C., and in 0.5 part of water at 100° C. It is soluble in 6 parts of alcohol at the ordinary temperature, and, when dissolved, if the addition of hydrochloric acid does not turn it brown, it is free from iodate. A solution of 1 part of potassium iodide in 2 parts of water will dissolve 2 parts of iodine, but upon dilution some of the iodine is precipitated.

Potassium Permanganate. $KMno_4$ (or $K_2Mn_2O_8$).

Potassium permanganate is a dark purple-red, anhydrous salt, crystallizing in long needles. It is soluble in 16 parts of water at 15° C. It is easily obtained very pure, but the solution should always be filtered through ignited asbestos, as paper has a strong reducing action on it.

Potassium Ferrocyanide. $K_4Fe_2Cy_6 + 3H_2O$.

Potassium ferrocyanide is a yellow, crystalline salt, soluble in 4 parts of water at 0° C., and in 2 parts of water at 100° C. It is used as a reagent to show the presence of ferric salts, which produce a blue coloration, caused by the formation of ferric ferrocyanide (Prussian blue).

Potassium Ferricyanide. $K_3Fe_2Cy_6$.

Potassium ferricyanide is a blood-red, anhydrous, crystalline salt, soluble in about 3.1 parts of water at 0° C., and in 1.3 parts of water at 100° C. The dilute solution, like that of the ferrocyanide, is yellow in color. Ferrous salts added to the solution give a blue coloration, due to the formation of ferrous ferricyanide, while ferric salts produce no change of color. The ferricyanide should never be kept in solution.

SALTS OF ALKALINE EARTHS.

Barium Carbonate. $BaCO_3$.

Barium carbonate prepared by precipitation is a soft white powder. It is difficult to obtain in a state of purity, but it is easily prepared by adding a solution of ammonium carbonate to a clear boiling solution of barium chloride, and washing the precipitated barium carbonate with hot water, first by decantation and afterwards on a filter. The ammonium carbonate should, of course, be free from sulphate. The thoroughly washed barium carbonate should be transferred to a bottle and shaken up with water, in which condition it is ready for use. Barium carbonate is very slightly soluble in water, requiring, according to the different authorities, from 4,000 to 25,000 parts of water to dissolve it. It is poisonous.

Barium Acetate. $Ba(C_2H_3O_2)_2$.

Barium acetate may be prepared by dissolving pure barium carbonate in acetic acid. It crystallizes with 1 or 3 molecules of water, but dried at 0° C., or exposed to the air, it effloresces and yields the anhydrous salt as a white powder. It is very soluble in water, dissolving in about 2 parts of water at 0° C., and in about 1 part at 100° C. When heated it decomposes into acetone and barium carbonate, thus:

$$Ba(C_2H_3O_2)_2 = C_3H_6O + BaCO_3.$$

Barium Chloride. $BaCl_2,2H_2O$.

Barium chloride is a white, crystalline salt, soluble in about 3 parts of water at 15° C., and in about 1½ parts at 100° C. Heated to 100° C. it loses its water of crystallization, yielding the anhydride as a white mass, which melts at a full red heat Barium chloride is almost insoluble in strong hydrochloric acid. It is used almost exclusively for the determination of sulphuric acid, and may be kept in solution for this purpose. 100 grammes of the crystallized salt dissolved in 1 litre of water is a good proportion to use. Of this solution 10 c.c. will precipitate 1.16 grammes of barium sulphate, equal to 0.4 gramme sulphuric anhydride or 0.16 gramme sulphur.

Caustic Baryta. Barium Hydroxide. $BaH_2O_2,8H_2O$.

Barium hydroxide is a white, crystalline salt, soluble in 20 parts of water at 15° C., and in 3 parts of water at 100° C. The anhydride may be prepared by heating barium nitrate to redness in a platinum crucible, raising the heat gradually at first to avoid loss from frothing. It attacks platinum, however, at a high temperature. The solution has a strong affinity for carbonic acid, absorbing it readily from the air, the barium carbonate so formed causing a scum on the surface of the solution. The solution attacks glass very strongly.

Calcium Chloride. $CaCl_2$.

Crystallized calcium chloride loses all its water of crystallization at 200° C., yielding the white porous anhydrous chloride, which is very deliquescent. The anhydrous salt fuses at a low red heat, but is partly changed to oxide. For this reason the fused salt should never be used for drying carbonic acid gas in the determination of this gas, as some of it is taken up by the calcium oxide. A solution of calcium chloride containing 59 parts of the anhydrous salt to 100 parts of water boils at 115° C., a saturated solution at 179.5° C.

Calcium Carbonate. $CaCO_3$.

Pure calcium carbonate, for use in Prof. J. Lawrence Smith's method for the determination of alkalies in silicates, is prepared as follows. Dissolve marble or calcite, free from magnesia, in dilute hydrochloric acid, add an excess of powdered marble, heat the solution, and add some milk of lime to precipitate magnesia, calcium phosphate, etc. Filter, heat the solution almost to boiling, and precipitate by ammonium carbonate. The calcium carbonate formed is a very dense powder, which settles readily and is easily washed. Wash thoroughly, dry, and preserve for use.

METALS AND METALLIC SALTS.

Metallic Copper.

Metallic copper absorbs chlorine gas at ordinary temperatures, and is used in iron analysis to absorb any chlorine that may be given off during the combustion of the carbonaceous matter liberated by the action of solvents on iron and steel. It is used in the form of drillings, which should be taken with a perfectly dry drill, and which should be free from oil and grease. The drillings should be kept in a stoppered bottle, and may be used as long as they are perfectly bright and clean.

Cupric Sulphate. $CuSO_4,5H_2O$.

Cupric sulphate is a blue, crystalline salt, soluble in 2.7 parts of water at 18° C., and in 0.55 part of water at 100° C. The aqueous solution of the neutral salt is strongly acid to litmus-paper. The crystals of cupric sulphate effloresce on the surface when exposed to the air; heated to 100° C. they lose 4 molecules of water, and when heated to 200° C. they lose the remaining molecule. The anhydrous salt is a white saline mass, which is decomposed at a bright red heat, giving off sulphurous acid and oxygen and leaving cupric oxide. The anhydrous salt has a strong affinity for water, and also for hydrochloric acid gas. A solution of cupric sulphate dissolves metallic iron, the copper being precipitated from the solution at the same time in a spongy mass.

Anhydrous Cupric Sulphate. $CuSO_4$.

The property anhydrous cupric sulphate possesses of absorbing hydrochloric acid gas makes it useful in the determination of carbon by combustion, and it is best prepared for this purpose as follows. Heat crystals of cupric sulphate, about the size of a coffee bean, in a porcelain dish until the blue color of the crystals disappears and they become white. Transfer while still hot to a dry, glass-stoppered bottle.

Anhydrous Cuprous Chloride. $CuCl$.

To prepare the granulated salt for use as an absorbent of hydrochloric acid and chlorine in carbon determinations, moisten the ordinary powdered salt of commerce in a porcelain dish and rub it up with a glass rod into little lumps about the size of a coffee bean. Heat it gradually until the water is expelled and the lumps, which will be dark brown in color, harden. Transfer to a glass-stoppered bottle.

Cupric Chloride. $CuCl_2 + Aq$.

To prepare cupric chloride for use in dissolving iron or steel for the determination of carbon, grind up equal weights of cupric sulphate and common salt in a porcelain mortar, and pour over the mixture a small amount of water heated to from 50° to 60° C. The liquid becomes emerald-green in color, and deposits upon evaporation sodium sulphate. Decant from the deposited salt and evaporate again until the solution is reduced to a very small bulk. Cool, and decant from the remainder of the sodium sulphate and the excess of sodium chloride. By further evaporation and cooling the cupric chloride may be obtained in the form of green crystals. These crystals are deliquescent. The solution should be diluted and filtered through asbestos.

Ammonium-Copper Chloride. $2(NH_4Cl),CuCl_2,2H_2O$.

Potassium-Copper Chloride. $2(KCl),CuCl_2,2H_2O$.

Ammonium-copper chloride is a bluish-green crystalline salt, quite soluble in water.

Potassium-copper chloride is bluish-green likewise and more soluble than the ammonium salt. The recent experiments of the American members of the International Steel Standards Committee have shown that ammonium-copper chloride is nearly always impure, from the presence of hydrocarbons in the ammonium chloride, derived probably from the gas liquor from which ammonia salts are distilled. These hydrocarbons unite with the carbonaceous residue liberated from steel and iron in the process of determining carbon, and of course vitiate the results. Several recrystallizations free the salt to a certain extent from this impurity. The use of the potassium salt is not open to this objection.

To prepare these salts proceed as follows. Dissolve 107 parts of ammonium chloride or 149.1 parts of potassium chloride and 170.3 parts of crystallized cupric chloride ($CuCl_2.2H_2O$) in water and crystallize out the double salt. Dissolve about 300 grammes of the double salt in 1 litre of water, filter through ignited asbestos, and preserve for use in glass-stoppered bottles.

Cupric Oxide. CuO.

Cupric oxide, both fine and coarse, for combustions is easily obtained. It may be prepared as follows. Dissolve metallic copper in nitric acid, evaporate to dryness in a porcelain dish, transfer it to a Hessian crucible, and heat it in a furnace until no more nitrous fumes are given off. Keep the crucible well covered to prevent any coal getting into it, and avoid raising the heat too high, or the mass will fuse. Stir it from time to time, and when finished the oxide on top will be in a fine powder, while that in the bottom of the crucible will have sintered. Rub it up in a mortar and pass through a fine metal sieve. Keep the two kinds, fine and coarse, in separate glass-stoppered bottles, carefully covered to protect them from dust.

Iron Wire.

Very fine soft piano-forte wire is the best form of iron to use when standardizing solutions of potassium permanganate or bichromate by metallic iron. Wrap one end of a piece of wire, about 2 feet (610 mm.) long around a lead-pencil, and, using this as a handle, draw the wire several times through a piece of fine emery-cloth, then through a fold of dry filter-paper, then, holding the wire with the paper, wrap it around the pencil. Cut off the end that has not been cleaned, and the little spiral of wire will be in a convenient form for weighing.

Ferrous Sulphate. $FeSO_4,7H_2O$.

Ferrous sulphate (green vitriol, or copperas) is a bluish-green crystalline salt, soluble in 1.64 parts of water at 10° C., and in 0.3 part at 100° C. It is insoluble in alcohol. The crystals lose 6 molecules of water when heated to 114° C., but retain the last molecule even at 280° C. Heated to a red heat the anhydrous sulphate is decomposed, giving off sulphurous acid and leaving a basic ferric sulphate, which at a higher temperature is entirely decomposed, leaving only ferric oxide. To prepare the crystals for use in volumetric analysis, add alcohol to the aqueous solution of the ferrous sulphate, when the salt is precipitated as a bluish-white powder. Filter, wash with alcohol, dry thoroughly, and preserve in glass-stoppered bottles. The salt prepared in this way remains unaltered for a long time.

Ferrous-Ammonium Sulphate. $FeSO_4(NH_4)_2SO_4,6H_2O$.

Ferrous-ammonium sulphate is a light green crystalline salt, soluble in 2.8 parts of water at 16.5° C. It may be prepared as follows. Dissolve 276 grammes of crystallized ferrous sulphate in water, filter, and add to the filtrate a clear solution of ammonium sulphate ($(NH_4)_2SO_4$, Glauber's Sal Secretum), evaporate down, and allow the double salt to crystallize out. Drain the crystals, wash slightly with cold water, and dry on blotting-paper. When perfectly dry, preserve in a glass-stoppered bottle. The crystals remain unaltered for a long time even in moist air. They contain exactly $\frac{1}{7}$ their weight of metallic iron.

Mercurous Nitrate. $HgNO_3,H_2O$.

To prepare this salt, pour cold, moderately strong nitric acid on an excess of metallic mercury, and when the violent action has subsided pour off the acid and allow the salt to crystallize out by the cooling of the acid. The salt is soluble in a small amount of water, but a large amount decomposes it into a basic salt and free acid.

Mercuric Oxide. HgO.

Mercuric oxide is a light orange-yellow substance when prepared by precipitation from a mercuric salt. To a dilute solution of mercuric chloride add a slight excess of caustic potash, allow the precipitate to settle, wash it thoroughly by decantation with hot water, and finally wash it into a glass-stoppered bottle. It is used shaken up with water.

Lead Chromate. $PbCrO_4$.

Fused lead chromate is a dark brown mass showing a radiated structure, and when powdered it is dark yellow in color, very heavy, and slightly hygroscopic. It is easily obtained very pure, but may be made as follows. Dissolve lead acetate in water, add a little acetic acid, filter, and precipitate by a solution of potassium bichromate. Wash by decantation, and finally on linen, dry, and heat in a Hessian crucible until the mass is just fused. Pour on a polished iron slab, grind in a clean mortar, and preserve the powder in glass-stoppered bottles, covered to exclude dust. Lead chromate heated to a full red heat gives off oxgyen and is reduced to a mixture of basic lead chromate and chromium oxide.

Lead Peroxide. PbO_2.

Lead peroxide is rather difficult to obtain in a state of purity; it is liable to contain lead nitrate and manganese oxide. The latter element interferes materially with its use as a reagent in the determination of manganese by the color test. It should always be carefully examined by boiling with dilute nitric acid, and, if it imparts any color to the solution, must be promptly rejected. It may readily be prepared by digesting red oxide of lead in dilute nitric acid, decanting off the lead nitrate, and washing the residue thoroughly with hot water. By this treatment the red oxide is decomposed into lead protoxide, which dissolves in the nitric acid, and lead peroxide, which remains insoluble. Lead peroxide is a heavy brown powder, which, when heated, gives off oxygen and is converted into red lead or lead protoxide.

Lead Oxide dissolved in Caustic Potash.

Pour a cold solution of lead nitrate into caustic potash, 1.27 sp. gr., stirring constantly to dissolve the lead oxide, which precipitates. Add the lead nitrate until a permanent precipitate is produced. Allow this to settle, and siphon the clear liquid into a glass-stoppered bottle. It is well to coat the stopper with a little paraffine, to prevent its sticking.

Platinic Chloride Solution.

Dissolve platinum-foil in hydrochloric acid, adding nitric acid from time to time, evaporate to dryness on the water-bath, redissolve in hydrochloric acid, and evaporate again to drive off the nitric acid. Redissolve in water with the addition of a few drops of hydrochloric acid, filter, and preserve in a bottle the stopper and neck of which are protected by a ground-glass cap to prevent access of ammonia to the solution.

Metallic Zinc.

Melt zinc, which should be as free as possible from lead and iron, in a Hessian crucible, and pour it in a thin stream from a height of four or five feet into a bucket of cold water, giving the crucible a circular motion to prevent the zinc from falling in exactly the same place all the time. Pour off the water, dry the granulated zinc, and preserve it in bottles for use.

Zinc Oxide in Water.

Emmerton * suggests the following method of preparing this reagent. Dissolve ordinary zinc white in hydrochloric acid, add the zinc white until there is an excess which will not dissolve, then add a little bromine-water, heat the solution, filter, and precipitate the zinc oxide by ammonia, being careful to avoid an excess. Wash thoroughly by decantation, and then wash into a bottle. Shake the bottle well, to diffuse the oxide through the water, before using.

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* Trans. Am. Inst. Min. Engineers, x. 201.

REAGENTS FOR DETERMINING PHOSPHORUS.

Magnesia Mixture.

Dissolve 110 grammes of crystallized magnesium chloride ($MgCl_2 + 6H_2O$) or 50 grammes of the anhydrous salt in water, and filter. Dissolve 28 grammes of ammonium chloride in water, add a little bromine-water and a slight excess of ammonia, and filter. Add this solution to the solution of magnesium chloride, add enough ammonia to make the solution smell decidedly of ammonia, dilute to about 2 litres, transfer to a bottle, shake vigorously from time to time, allow it to stand for several days, and filter into a small bottle as required for use. 10 c.c. of this solution will precipitate about 0.15 gramme phosphoric acid.

Molybdate Solution.

Weigh 100 grammes of pure molybdic anhydride, mix it thoroughly in a beaker with 400 c.c. of cold distilled water and add 80 c.c. of strong ammonia (0.90 sp. gr.). When solution is complete, filter and pour the filtered solution slowly with constant stirring into a mixture of 400 c.c. of strong nitric acid (1.42 sp. gr.) and 600 c.c. of distilled water. Allow to settle for 24 hours and filter. A solution prepared in this way will keep for several months even in hot weather without any deposition of molybdic acid.

METHODS FOR THE ANALYSIS

OF

PIG-IRON, BAR-IRON, AND STEEL

DETERMINATION OF SULPHUR.

By Evolution as Hydrogen Sulphide.

KARSTEN was the first to suggest dissolving iron or steel in hydrochloric acid, or dilute sulphuric acid, and collecting the evolved hydrogen sulphide by absorbing it in a solution of a metallic salt. He recommended cupric chloride.

Absorption by Alkaline Solution of Lead Nitrate.

The apparatus, Fig. 47, shows the usual arrangement for carrying out the process, with the addition of the generating-bottles for supplying hydrogen gas. This is the apparatus described under the head of "Apparatus for Generating Carbonic Acid Gas," page 42. The wash-bottle A contains an alkaline solution of lead nitrate, and is connected with the funnel-tube by the rubber tube B, and a small piece of glass tubing, C, turned at a right angle with one end drawn down and covered with a short piece of rubber tubing. This fits in the neck of the bulb of the funnel-tube and makes a tight joint. The analytical process is conducted as follows:

Place 10 grammes* of borings or drillings, free from lumps, in the reviously dried flask D, and close it with the rubber stopper fitted with funnel-tube and a delivery-tube. The outlet-tube from the flask D

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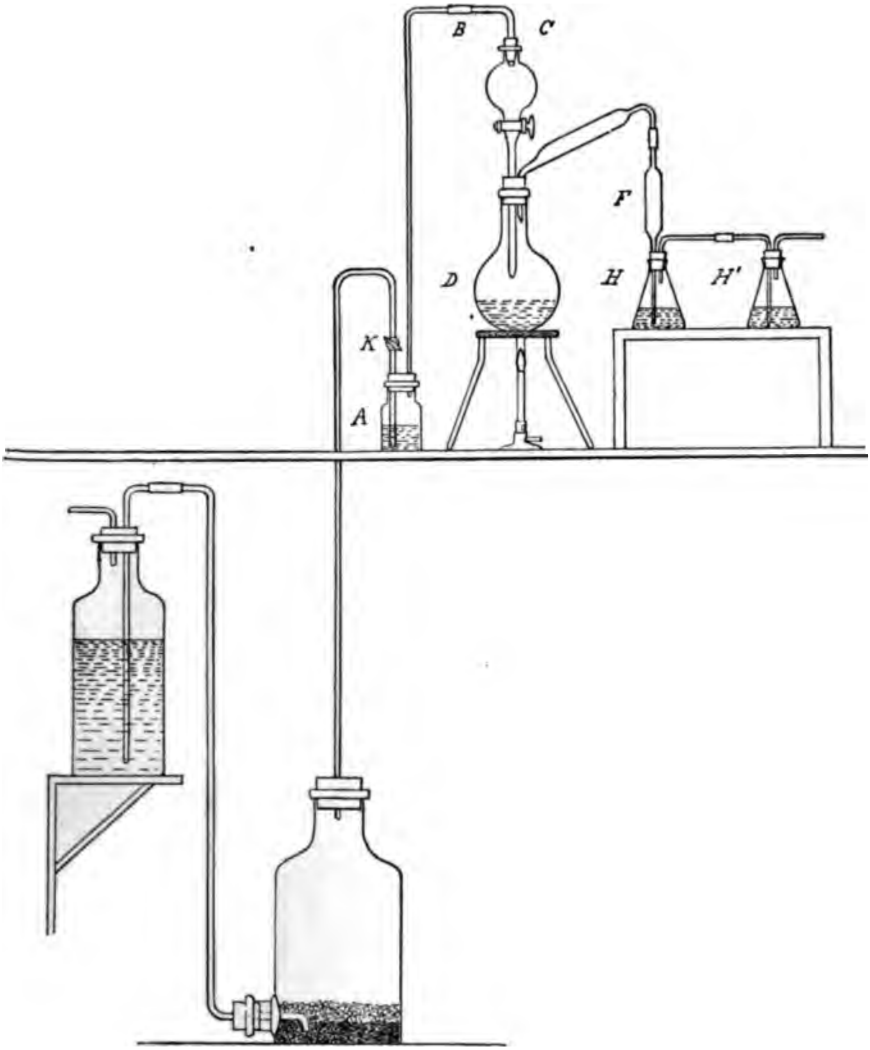
* A 5-factor weight (6.878 grammes) is a better amount to take, as, when the weight of barium sulphate found is multiplied by two, each milligramme is one-thousandth of a per cent. of sulphur.

FIG. 47.



onnects with the tube F, reaching almost to the bottom of the Erlenmeyer flask H. Pour into each of the flasks H about 20 or

30 c.c. of potassium hydrate solution of lead nitrate * and enough water to fill them two-thirds full. Connect the apparatus, and run a slow stream of hydrogen through until all the air is expelled, then close the glass stopcock of the funnel-tube, and shut off the supply of hydrogen by closing the small glass stopcock K. If the connections are all tight, the liquid will not recede in the tube F. When this is assured, disconnect the tube C, and fill the bulb—which should be of about 100 c.c. capacity—with a mixture of 50 c.c. of strong hydrochloric acid and 50 c.c. of water. Replace the tube C, turn on the hydrogen, and open the stopcock of the funnel-tube, so as to allow the acid to flow into the flask D. When the acid has all run into the flask, regulate the flow of the hydrogen so that the gas shall pass through the solutions in the flasks H, H′ as rapidly as possible, and heat the flask D. When the solution in the flask D has boiled for fifteen minutes, and all the metal has dissolved, remove the source of heat and continue the current of hydrogen for about ten minutes, regulating its flow by means of the stopcock K, to prevent any reflux of the liquid in H, which might be caused by the cooling of the flask D. Shut off the hydrogen, disconnect the apparatus, and wash the contents of the flask H into a No. 2 Griffin's beaker. Unless a precipitate of lead sulphide appears in the second flask H′, it need not be emptied, but the same solution can be used over again for the next analysis. Collect the precipitate on a small filter, wash it once or twice with hot water, and, while still moist, throw the filter and precipitate back into the beaker, in which have been placed the instant before some powdered potassium chlorate and from 5 to 20 c.c. of strong hydrochloric acid, according to the amount of the precipitate of lead sulphide. Allow it to stand in a warm place until the fumes shall have partly passed off, then add about twice its volume of hot water, and filter into a No. 1 beaker. Wash with hot water, heat the filtrate to boiling, and add ammonia until the solution is slightly alkaline to litmus-paper. Acidulate with a few drops of hydrochloric acid, add from 5 to 10 c.c. of barium

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* See page 58.

chloride solution,* boil 15 or 20 minutes, and stand aside for half an hour. Filter the precipitate of barium sulphate, preferably on a Gooch perforated crucible, wash with hot water, ignite, and weigh as barium sulphate, which contains 13.75 per cent. sulphur. It is always well to test the alkaline filtrate from the lead sulphide with a few drops of the lead solution, for it might happen that all the lead would be precipitated from the solution as sulphide, and an excess of hydrogen sulphide remain in the solution as potassium sulphide.

The entire operation described above can be performed in about two and a half hours, and is, in my opinion, the most accurate method known for the determination of sulphur in steel.

Absorption by Ammoniacal Solution of Cadmium Sulphate.

T. T. Morrell † passes the evolved gas into an ammoniacal solution of cadmium sulphate. Prepare a solution of cadmium sulphate of convenient strength, and add enough ammonia to redissolve the precipitate and give a clear solution. Place the solution in the bottles H, H′, and proceed as usual. Filter the precipitate of cadmium sulphide in a counterpoised filter, wash with water containing a little ammonia, dry at 100° C., and weigh as cadmium sulphide, which contains 22.25 per cent. of sulphur. Instead of cadmium sulphate, cadmium chloride seems to be now more generally in use.

Absorption by Ammoniacal Solution of Silver Nitrate.

Berzelius proposed the use of a dilute solution of silver nitrate made alkaline by ammonia. The method of procedure is as follows. Dissolve 1 gramme of silver nitrate in a small quantity of water, and make it strongly alkaline with ammonia; pour about two-thirds of the solution into the first of the bottles H, and the remainder into the second, and fill up to the proper level with water. Proceed exactly as described above until the silver sulphide has been filtered off and washed. Dry this precipitate carefully at a low temperature—say 100° C.—and brush it carefully into a small, dry beaker, returning the filter to the funnel. Pour into the bottles H, should any of the sulphide remain adhering to the sides, 20 or 30 c.c. strong nitric acid, and when it is all dissolved, pour the acid in the filter, allowing it to run into the beaker containing the silver sulphide, and wash out the bottles with a little nitric acid, allowing this to run over the filter also. Digest the silver sulphide until it is all dissolved, then dilute with hot water, add an excess of hydrochloric acid, and filter off the silver chloride. Add a small amount of sodium carbonate, and evaporate nearly dry, dilute, add a few drops of hydrochloric acid, filter if necessary, and precipitate as before by barium chloride. Even when the sample contains no sulphur a slight precipitate of silver carbide may be thrown down by the carburetted hydrogen evolved from the iron or steel by the action of the acid.

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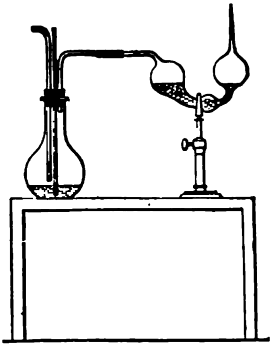
* See page 51.

† Chem. News, xxviii. 229.

Absorption and Oxidation by Bromine and Hydrochloric Acid.

Fresenius * suggested passing the evolved gases through a solution of bromine in hydrochloric acid, which has the advantage of oxidizing the hydrogen sulphide at once, but the disadvantage of filling the room with bromine-fumes unless the apparatus is placed under a hood with a good draft. It is necessary when using this method to avoid bringing the bromine-fumes in contact with rubber stoppers. Instead of the bottles H, attach to the exit-tube a bulb-tube of the shape shown in Fig. 48, containing from 3 to 5 c.c. of bromine and enough hydrochloric acid to fill the bulb-tube to the marks shown in the cut. When the operation is finished, wash the contents of the bulb-tube out into a beaker, heat until the bromine is all driven off, neutralize by ammonia, and precipitate the sulphuric acid exactly as described on page 62. Instead of neutralizing by ammonia, the hydrochloric

FIG. 48.



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[*] Fresenius, Zeitschrift, xiii. 37.

acid solution may be evaporated down nearly to dryness after adding a little sodium carbonate or the solution of barium chloride; but repeated experiments have shown that barium sulphate is practically insoluble in ammonium chloride, so that the plan of neutralizing by ammonia, being the shorter and less troublesome, is to be preferred.

Absorption and Oxidation by Potassium Permanganate.

Drown * suggested the use of potassium permanganate solution as an absorbent and oxidizer, the process being carried on as follows. Make a solution of potassium permanganate, 5 grammes to the litre of water, and fill the bottles H to the proper height with this liquid, using three bottles, however, instead of two, and proceed with the operation as before described, being careful to avoid a rapid evolution of the gas. Wash the contents of the bottles H into a clean beaker, dissolve any manganese oxide that may adhere to the sides of the bottles in hydrochloric acid, add this to the solution in the beaker, and then add enough hydrochloric acid to entirely decompose the permanganate. Boil until the solution is colorless, filter if necessary, and precipitate by barium chloride. Allow it to stand overnight, filter, wash, ignite, and weigh the barium sulphate.

Absorption and Oxidation by Hydrogen Peroxide.

Craig † suggested the use of ammoniacal solution of hydrogen peroxide in the absorbing-bottles. Attach to the exit-tube of the flask D (Fig. 47) a nitrogen-bulb of the usual form (Fig. 48), in which have been placed 4 c.c. of hydrogen peroxide and 16 c.c. of ammonia, and proceed as before directed. When the operation is finished, wash the contents of the nitrogen-bulb into a small beaker, acidulate slightly with hydrochloric acid, boil, add barium chloride, and determine the amount of barium sulphate as usual. As hydrogen peroxide always contains sulphuric acid, the amount must be carefully determined in each fresh lot of the hydrogen peroxide, and the proper correction made for the volume used.

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* Journal Inst. Min. Engineers, ii. 224.

† Chem. News, xlvi. 199.

By Oxidation and Solution.

Many chemists still prefer the method of oxidizing and dissolving the metal and precipitating the sulphuric acid in the solution by barium chloride. The details are as follows. Treat 5 grammes of drillings in a No. 4 Griffin's beaker, covered by a watch-glass, with 40 c.c. of strong nitric acid. This requires care, for drillings of bar-iron and low steel are often acted on so violently, even by strong nitric acid, as to cause the solution to boil over. In this case it is best to place the beaker in a dish containing a little cold water and to add the acid gradually. When all the acid has been added and the action has ceased, some small particles generally remain undissolved, and their solution is effected by heating the beaker on the sand-bath and finally by adding a few drops of hydrochloric acid. With pig-iron and steel there is usually no action in the cold, and in this case heat the beaker carefully until the action begins, then stand the beaker in a cooler place, and if the action becomes very violent, stand the beaker in cold water until it moderates. Very high carbon steels dissolve with great difficulty even in boiling acid; but the solution may be hastened by adding a few drops of hydrochloric acid from time to time. When solution is complete and only particles of graphite and silica remain undissolved, which is shown by the residue being entirely flotant, remove the cover, add a little sodium carbonate, and evaporate the solution to dryness in the air-bath. The addition of the sodium carbonate is to prevent any possible loss of sulphuric acid, which might otherwise occur by the decomposition of the ferric sulphate at a high temperature. Remove the beaker from the air-bath, and when cold add 30 c.c. hydrochloric acid, and heat until the ferric oxide is dissolved, evaporate again to dryness to render the silica insoluble, redissolve in hydrochloric acid, evaporate until the ferric chloride begins to separate out, add 2 c.c. hydrochloric acid and a little water. Filter and wash, being careful that the total filtrate and washings shall not exceed 100 c.c. in volume. Heat the filtrate to boiling, add 10 c.c. saturated solution of barium chloride, and allow it to stand in the cold overnight. Filter, wash with a little very dilute hydrochloric acid, and finally with cold water; dry, ignite, and weigh as barium sulphate. If this ignited precipitate is reddish in color, it shows that ferric oxide has been precipitated with the barium sulphate. In this case fuse with sodium carbonate, dissolve in water, filter, acidulate the filtrate, and precipitate as before. Or, filter the aqueous solution of the fusion, dissolve in hydrochloric acid, precipitate by ammonia, weigh the ferric oxide, and subtract from the weight of barium sulphate.

Bamber's Method (for Pig-Iron).

The investigations of Phillips * and Matthewman † have shown conclusively that in many pig-irons the evolution method fails to give the full sulphur contents. This seems to be due to the formation of organic sulphides, probably of the mercaptan series, and not to the presence of copper or arsenic, as has been supposed. As those compounds are quite volatile and very difficult to oxidize, some portions seem to pass through the absorbing solutions, while under certain circumstances other portions remain in the evolution flask with great persistency and are expelled only after long boiling.

The only practicable method for pig-irons of this character, therefore, is the following. Dissolve 5 grammes or a 5-factor weight (6.878 grammes) in strong nitric acid, add 10 grammes of sodium carbonate, wash into a platinum or porcelain dish, evaporate to dryness and ignite over an alcohol flame. Treat with water with the addition of a little sodium carbonate, filter, and wash with water containing sodium carbonate. Acidulate with hydrochloric acid, evaporate to dryness, redissolve in water with a few drops of hydrochloric acid, and precipitate boiling with barium chloride.

Notes and Precautions.

There are three precautions to be observed in using the oxidation method.

1. The sample should be dissolved in strong nitric acid, as, when dilute nitric acid, or even aqua regia, is used, some sulphur seems to escape oxidation.

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* Journal American Chem. Society, xvii. 891.

† Journal West of Scotland Iron and Steel Institute, iii. 27.

2. The amount of acid in the solution from which the barium sulphate is precipitated must be most carefully regulated, as well as the absolute volume of the solution.

3. The reagents used must be examined for sulphuric acid. This is best done as follows. Measure into a beaker the total amount of acid, both nitric and hydrochloric, used in the determination, add a little sodium carbonate and evaporate to dryness. Redissolve in 15 c.c. of water and 5 or 10 drops of hydrochloric acid, filter, heat to boiling, add 10 c.c. of barium chloride, boil 10 or 15 minutes, allow to settle, filter, wash, ignite, and weigh as barium sulphate. The amount found is to be subtracted from the total weight of barium sulphate found in the sample.

In the use of the evolution method for steels, the results obtained vary somewhat with the solution used for absorbing the hydrogen sulphide, and I am satisfied that the best absorbent is the alkaline solution of lead nitrate. I have never failed, so far as I know, in getting correct results with this absorbent in any steel. The evolution of the gas should be as rapid as possible, as there seems to be no danger of any hydrogen sulphide passing the liquid in the first flask, and the operation is naturally shortened. If the solution containing the precipitated barium sulphate is boiled vigorously for 15 or 20 minutes, it is not necessary to allow it to stand more than half an hour, so that a determination can be made in two hours, or two hours and a half, without any trouble.

RAPID METHOD.

Volumetric Determination by Iodine.

This method, suggested by Elliott,* involves the evolution of the sulphur as hydrogen sulphide, its absorption in a solution of sodium hydroxide, and titration by iodine in potassium iodide. It requires a standard solution of iodine, a standard solution of sodium thiosulphate, a starch solution, and a standard solution of potassium bichromate.

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* Chem. News, xxiii. 61.

Iodine Solution.

Dissolve 6.5 grammes pure iodine in water with 9 grammes potassium iodide, and dilute to 1 litre.

Sodium Thiosulphate Solution.

Dissolve 25 grammes sodium thiosulphate in water, and dilute to 1 litre.

Starch Solution.

Weigh into a porcelain or Wedgwood mortar 1 gramme of pure wheat starch, and rub it to a thin cream with water. Pour it into 150 c.c. boiling water, allow it to stand until cold, and decant the clear solution. The addition of 10 or 15 c.c. glycerine makes the solution keep better. It is better, however, to make a fresh starch solution every few days.

Dr. Waller recommends Müller's suggestion of grinding the starch with a strong solution of potassium or sodium hydroxide and dissolving in hot water for use. It keeps indefinitely.

Potassium Bichromate Solution.

Dissolve 5 grammes pure potassium bichromate in water, and dilute to 1 litre.

All these solutions should be placed in glass-stoppered bottles and kept in a dark place.

Standardizing the Solutions.

Standardize the bichromate solution as directed in the "Analysis of Iron Ores." When potassium bichromate is added to potassium iodide in presence of free hydrochloric acid, iodine is liberated, in accordance with the formula $K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + Cr_2Cl_6 + 7H_2O + 6I$, or 1 equivalent of potassium bichromate = 294.5 liberates 6 equivalents of iodine = 761.1. Therefore, by adding to a solution of potassium iodide in the presence of hydrochloric acid a known amount of bichromate, we can calculate the absolute amount of iodine liberated, and by titrating this solution by the thiosulphate solution we can accurately standardize the latter. The reaction which takes place when a solution of sodium thiosulphate is acted on by iodine is $2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$, or 2 equivalents of thiosulphate unite with 2 equivalents of iodine to form sodium iodide and sodium tetrathionate. By adding a few drops of starch solution to a solution containing iodine, blue iodide of starch is formed, and colors the solution as long as it contains free iodine. When enough thiosulphate is added to a solution of this kind to combine exactly with the iodine, the blue color disappears. Conversely, upon adding a solution of iodine to a solution containing sodium thiosulphate and a little starch, the sensitive blue color of the iodide of starch will disappear as fast as formed until all the thiosulphate has been changed to tetrathionate, and then the first drop of iodine in excess will change the solution to a permanent blue. The same thing holds true as regards a solution containing free hydrogen sulphide, the reaction being $H_2S + 2I = 2HI + S$. Proceed therefore as follows. Dissolve about 1 gramme of pure potassium iodide in 300 c.c. water, add 5 c.c. hydrochloric acid, and then 25 c.c. of the bichromate solution, which will liberate a known amount of iodine. Drop in now the thiosulphate solution from a burette until the iodine nearly disappears, add a few drops of starch solution, and continue the thiosulphate until the blue color fades out entirely. The amount of iodine being known, the value of the thiosulphate solution is calculated from the reading of the burette. Now allow to flow into a beaker from a carefully graduated pipette 25 c.c. of the thiosulphate solution, dilute to 300 c.c., add a few drops of the starch solution, and drop, from a burette, standard iodine solution until the blue color is permanent. The value of the thiosulphate solution being known, that of the iodine solution is readily calculated. An example will illustrate this. Suppose we find by titration that 1 c.c. of our bichromate solution is equal to .00566 gramme metallic iron; then, as the reaction is $6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O$, 1 equivalent of potassium bichromate = 294.5 is equal to 6 equivalents of iron = 336. Hence 336 : 294.5 = .00566 : .004961, or 1 c.c. of the bichromate solution contains .004961 gramme potassium bichromate, and consequently 25 c.c. contain .124025 gramme potassium bichromate. Then, as we saw by the formula that 294.5 parts bichromate liberate 761.1 parts iodine, we have 294.5 : 761.1 = .124025 : .32052, or 25 c.c. of the bichromate solution liberate .32052 gramme iodine. We now find that it requires 25.3 c.c. of the thiosulphate solution to decolorize the solution made by adding 25 c.c. bichromate solution to the potassium iodide; consequently each c.c. of the thiosulphate contains enough sodium thiosulphate to react with .01267 gramme iodine. We now measure out 10 c.c. of the thiosulphate solution, dilute it to 300 c.c., add a few drops of starch solution, and find that it requires 20.1 c.c. of the iodide solution to give the permanent blue color. Hence 20.1 c.c. = .1267 gramme iodine, or 1 c.c. iodide solution contains .006303 gramme iodine. As the reaction with hydrogen sulphide is $H_2S + 2I = 2HI + S$, it requires 2 equivalents of iodine to decompose 1 equivalent of hydrogen sulphide, and the proportion is 2I : S : : 253.7 : 32.06 : : .006303 : .000796, or 1 c.c. iodine is equal to .000796 gramme sulphur.

The standard solutions once ready, the actual determination of sulphur in a sample is very simple. Pour 50 c.c. of a solution of caustic soda, 1.1 sp. gr., free from sulphur, into the first of the bottles H. The second need not be used, but it is a good plan to keep a caustic potash solution of lead nitrate in it, and attach it after the other, to be certain that no hydrogen sulphide escapes the caustic soda solution. Proceed with the determination as directed on page 60, and when finished wash the contents of the bottle H into a beaker, dilute to 500 c.c., acidulate with hydrochloric acid, add a few drops of starch solution, and titrate with the iodide solution. See exactly how much hydrochloric acid is required to acidulate strongly 50 c.c. of the caustic soda solution, and this amount can be added at once, so that no time need be lost in testing the solution with litmus before titrating.

Mr. E. F. Wood,* of the Homestead Steel-Works, modifies the method as follows. Pass the evolved gas into an ammoniacal solution of cadmium sulphate instead of caustic soda. Filter, place the filter containing the precipitate of cadmium sulphide in a beaker containing cold water, add enough hydrochloric acid to dissolve the precipitate, and titrate with iodide solution as above described.

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* Communicated to the author.

Mr. Wood thinks that this method has several advantages over that in which caustic soda is used to absorb the hydrogen sulphide. The hydrocarbon gases absorbed by the alkaline solution are gotten rid of, and the error which their presence may produce is avoided; the bulk of the precipitate is an indication of the amount of sulphur and a guide to the proper amount of hydrochloric acid to use for its solution, and when the cadmium sulphide is filtered off, only a small amount of hydrochloric acid is required, and the generation of heat from the neutralization of the alkali is avoided.

DETERMINATION OF SILICON.

By Solution in Nitric and Hydrochloric Acids.

Dissolve 5 grammes of drillings in 40 c.c. nitric acid with the precautions mentioned on page 66; although when silicon *alone* is to be determined, nitric acid of 1.2 sp. gr. may be used, when, in most cases, the solution of the drillings will be more rapid. Remove the cover, evaporate the solution to dryness in the air-bath, replace the cover, and raise the temperature of the bath until the ferric nitrate is decomposed. Remove the beaker from the air-bath, allow it to cool, add 30 c.c. hydrochloric acid, and heat gradually until all the ferric oxide is dissolved. Remove the cover, and evaporate again to dryness in the air-bath, redissolve in 30 c.c. hydrochloric acid, dilute to about 150 c.c., and filter on an ashless filter. Detach any adhering silica from the sides and bottom of the beaker with a "policeman," or with a piece of filter-paper, and wash it out with cold water. Wash the filter first with dilute hydrochloric acid, and finally with water. Dry, and ignite in a platinum crucible until all the carbon is burned, weigh the residue in the crucible, moisten it with water, add from 1 to 10 drops sulphuric acid, and enough hydrofluoric acid to dissolve it completely, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica, which contains 47.02 per cent. of silicon. In the absence of hydrofluoric acid, unless the silica is perfectly white, fuse with 5 or 6 times its weight of sodium carbonate, dissolve in water, acidulate with hydrochloric acid, evaporate to dryness (in a platinum or porcelain dish, with the arrangement shown on page 20), redissolve in hydrochloric acid and water, dilute, filter, wash, ignite, and weigh. When the weight of sodium carbonate taken does not exceed 2 or 3 grammes, allow the crucible to cool after fusion, and then add to it gradually an excess of strong sulphuric acid, heating very slowly, until the mass is quite liquid and fumes of sulphuric anhydride come off. Allow it to cool, dissolve in water, filter, wash well, ignite, and weigh.

By Solution in Nitric and Sulphuric Acids.

Drown [*] has suggested a method which, for pig-irons, has come into very general use, and which is much more rapid than the other method and quite as exact. Treat 1 gramme of borings in a platinum or porcelain dish with 20 c.c. nitric acid, 1.2 sp. gr. When all action has ceased, add 20 c.c. of sulphuric acid (equal parts of acid and water), and evaporate—using the arrangement shown on page 20—until copious fumes of sulphuric anhydride are given off. Allow to cool, and dilute with 150 c.c. water; heat carefully until all the ferric sulphate has dissolved, filter hot,[†] wash first with dilute hydrochloric acid, 1.1 sp. gr., and then with hot water, ignite, and weigh. Treat the contents of the crucible with sulphuric and hydrofluoric acids, evaporate to dryness, ignite, and weigh again. The difference between the two weights is silica.

By Volatilization in a Current of Chlorine Gas.

As almost all steels and irons contain slags of various compositions, it must be understood that the silica obtained by the methods given above is the total silica, comprising any silica that may be present in

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[*] Journal Inst. Min. Engineers, vii. 346.

[†] Dr. Dudley has shown that upon long standing silica dissolves, and it is therefore advisable to filter the sulphuric acid solution as soon as the ferric sulphate is dissolved.

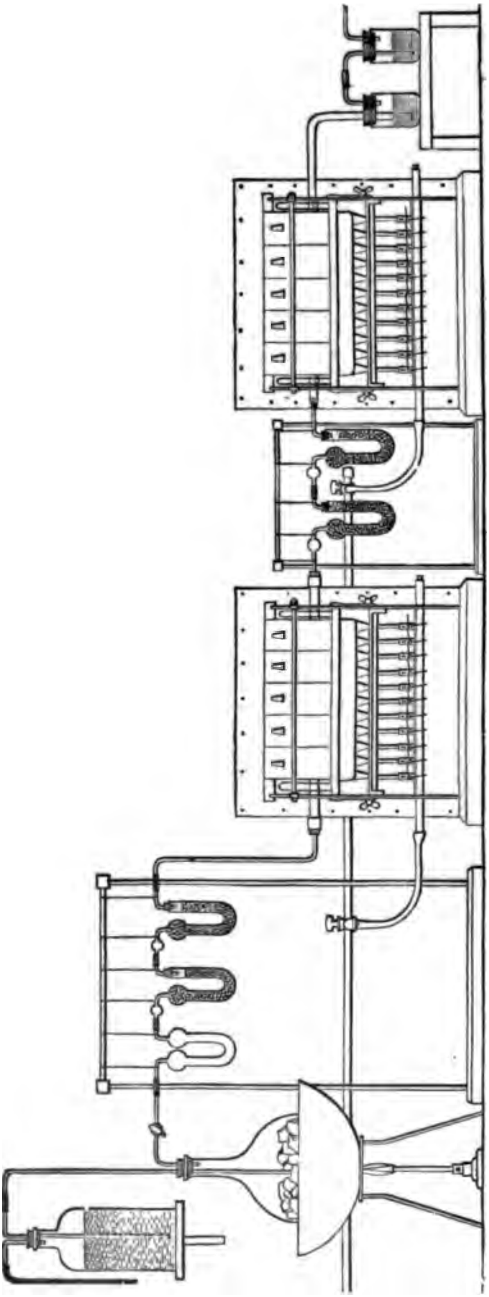

FIG. 49.

the admixed slag, as well as that formed from the silicon present in the metal. The volatilization method separates the two. The process suggested by Drown,* and worked out independently two years later by Watts,† is as follows. Fig. 49 shows the general arrangement of the apparatus. The large flask contains strong common manganese dioxide in lumps. The bottle above it contains strong common hydrochloric acid, which runs into the flask through a siphon-tube extending almost to the bottom. The flask stands in a dish containing water, which can be heated by the burner under the tripod. The evolution-tube from the flask has a stopcock, and connects with the three bulb-tubes on the stand, the first containing water, the second pumice-stone, and the third pumice saturated with strong sulphuric acid. The outlet-tube from the latter leads into the porcelain or glass tube in the furnace. This tube contains small lumps of charcoal or gas carbon, kept in position by loosely fitting plugs of asbestos, and occupying about 8 inches (200 mm.) in the middle of the tube. The outlet-tube from this connects with the drying-tubes on the second stand, which contain pumice moistened with strong sulphuric acid. The outlet from the second drying-tube connects with the glass combustion-tube, which leads through the second furnace, and is bent at a right angle where it is connected with the large tubes, half filled with water. The apparatus being in order, ‡ start a slow current of chlorine through the apparatus by blowing hydrochloric acid from the bottle into the flask and filling the dish in which the latter stands with water. Light a low light under the dish, and open the stopcock wide enough to allow a very slow current to bubble through the bulbs. Light the burners of the first furnace so that the tube is heated to dull redness. When the apparatus is full of chlorine, place 1 gramme of pig-iron, or 3 grammes of steel, in a porcelain boat about 3 inches long, distributing the drillings evenly along the bottom of the boat. Remove the stopper at the rear end of the second tube and insert the boat to about the centre. Replace the stopper, and continue the current of chlorine in the cold for ten or fifteen minutes to make sure that no oxygen remains in the tube, then light the burner under the forward end of the boat. The heat must be just sufficient to volatilize the ferric chloride, which should condense in the cooler part of the tube, and the current of gas should be slow enough to prevent any ferric chloride from being carried forward into the water-tubes or any loss of carbon from the boat. When the fumes of ferric chloride begin to come off more slowly, light the next burner, and continue until all the burners under the boat are lighted, maintaining the heat until the fumes of ferric chloride cease. The tube for the entire length occupied by the boat should be at a dull red heat. Should the condensed ferric chloride at any time choke the tube so as to prevent the passage of the gas, heat that part of the tube gently with a spirit-lamp, so as to drive the ferric chloride a little farther along the tube. When the fumes of ferric chloride are no longer given off from the boat, the operation may be considered finished. Turn out the lights under the tube containing the boat, remove the stopper, and draw out the boat, which now contains the carbon, the slag, and the greater part of the manganese (as chloride) which were contained in the iron and steel. This residue may be used for the determination of the carbon or the slag, as will be shown farther on. If another determination is to be made, another tube may be substituted for the one which contained the boat, and the analysis carried out in the manner described above. If not, put out all the lights, close the stopcock, and withdraw the combustion-tube with the water-tubes. Remove the stoppers from the latter, and pour the contents of these tubes into a platinum dish containing a small amount of an aqueous solution of sulphurous acid, to prevent the chlorine in the solutions from acting on the platinum. Rinse the tubes into the dish, and if any silica has separated and adheres to the water-tubes or to the end of the combustion-tube, loosen it with a "policeman" and wash it into the dish. Add 5 c.c. strong sulphuric acid, evaporate to dryness, and heat until fumes of sulphuric anhydride are given off. Allow the dish to cool, add 100 c.c. cold water, and filter the silica on a small ashless filter. Burn and weigh as silica. Calculate to Silicon. The filtrate from the silica will contain any titanic acid which may have been in the metal and which can be determined, as will be shown farther on. Silicon and titanium are volatilized as chlorides, under the conditions shown above, and decomposed by water thus: $SiCl_4 + 2H_2O = 4HCl + SiO_2$ and $TiCl_4 + 2H_2O = 4HCl + TiO_2$.

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* Jour. Inst. Min. Engineers, viii. 508.

† Chem. News, xlv. 279.

‡ All the stoppers used should be of rubber coated with paraffine on the ends, or of asbestos, and where glass tubes are joined together with rubber the ends of the glass tubes should be brought into close contact.

Rapid Method for Determination of Silicon. (S. Alfred Ford.*)

At the Edgar Thomson Steel-Works the molten pig-metal is taken directly from the furnaces to the converters, and it is generally necessary to determine the amount of silicon in the pig-iron as a guide in blowing the metal. To get the sample for analysis, a small ladle is dipped into the iron as it runs from the furnace, and a small quantity of molten iron is taken. The ladle is then held about three feet above a bucket of water, and the molten metal dropped into the water, at the same time giving the ladle a circular motion over the bucket. This will cause the iron to form in globules, more or less round according to the amount of silicon contained in the iron. Thus, with iron which contains 2 per cent. of silicon or more, the globules will be almost perfectly round, concave on the upper surface, and generally from ¼ inch (6 mm.) to ⅜ inch (9 mm.) in diameter; while if the iron be low in silicon, the shot or drops will be very small, flat, and irregular in shape, and if the iron be very low in silicon, as is the case with spiegel and ferro-manganese, the shot will be elongated and have tails sometimes ¼ inch (6 mm.) in length. In fact, a close observer can soon judge very closely as to the amount of silicon from the condition of these shot or drops. The next step in the process is to take the shot from the bucket and place them for a minute in the ladle which has been used to dip up the molten iron. The ladle, being hot, will dry the shot almost instantly. The shot are then placed in a large steel mortar (Fig. 7, page 17) and crushed. The crushed shot are then sifted with a fine sieve, and

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* Prepared by Mr. Ford for this volume.

.5 gramme of the fine siftings are placed in a platinum evaporating-dish, 10 c.c. hydrochloric acid, 1.2 sp. gr., are then added, and the dish covered with a watch-glass. The dish is then placed over a light, and the iron dissolved; as soon as solution takes place, which requires about one minute, as the particles of iron are so small, the watch-glass is removed and the solution evaporated to dryness as rapidly as possible over a naked light; as soon as dry, not even waiting for the dish to cool, dilute hydrochloric acid is dropped on the ferric chloride, and as soon as all the ferric oxide (which may have been formed by the decomposition of the chloride) is dissolved, water is added. The contents of the dish are then poured on a filter, to which is attached a pump, filtered, and washed. The filter and its contents are then placed in a weighed platinum crucible, placed over a blast-lamp; as soon as the filter-paper is burned off, the crucible is turned on its side, the lid removed, and a small jet of oxygen is driven very gently into the crucible. As soon as what little carbon there is in the precipitate is burned off, the crucible is cooled and weighed, and the amount of silicon calculated from the weight of the silica in the crucible.

By this method the amount of silicon in a pig-iron can be determined in twelve minutes from the time the ladle is put into the molten iron, and it gives results close enough for practical purposes.

DETERMINATION OF SLAG AND OXIDES.

A certain amount of slag and oxide of iron is always present in puddled iron as a mechanical admixture. It is also found, as a general thing, in basic steel, and the presence of slag in steel made by the acid process, as well as in pig-iron, is not unusual. The easiest method for the determination of these substances is by solution in iodine, as suggested by Eggertz.

By Solution in Iodine.

Place 5 grammes of borings free from lumps in a No. 2 Griffin's beaker. Stand the beaker, carefully covered with a watch-glass, in a dish filled with scraped ice or snow, so that the bottom and sides of the beaker half-way up shall be in contact with it. Pour over the iron in the beaker

25 c.c. of ice-cold boiled water, and stir until all the air in the borings has escaped. Add gradually from 28 to 30 grammes of resublimed iodine,* stirring occasionally, until all the iodine has dissolved. Keep the beaker constantly surrounded by ice, and add the iodine slowly enough to prevent any rise in the temperature of the solution. Stir the solution frequently until the iron is perfectly dissolved, which will take several hours; then add 100 c.c. cold boiled water, allow the insoluble matter to settle, and decant the supernatant fluid on a small ashless filter. Wash the insoluble matter several times, by decantation, with cold water, then add to it a little water, with a few drops of hydrochloric acid, and observe whether any hydrogen is disengaged. If none can be perceived, the metallic iron may be considered entirely dissolved; but if gas is given off, the opposite is the case. In either event, quickly decant the acidulated water on the filter, and if any metallic iron remains, add a very little water and some iodine to dissolve the iron entirely. Then transfer the insoluble matter, consisting of graphite, carbonaceous matter, slag, iron oxide, and some silica, to the filter, wash the filter once with very dilute hydrochloric acid (1 acid to 20 water), and finally with cold water, until the filtrate is free from iron. Unfold the filter, and with a fine jet wash off the insoluble matter into a small platinum or silver dish. Evaporate almost to dryness, add 50 c.c. solution of caustic potash, sp. gr. 1.1, and boil five or ten minutes. Decant the liquid on a very small ashless filter, repeat the boiling with fresh caustic potash, transfer the insoluble matter to the filter, and wash well with hot water. Wash once with dilute hydrochloric acid (1 acid to 20 water), and finally with hot water, until the filtrate gives no precipitate with a solution of silver nitrate. Dry, ignite, and weigh as Slag and Iron Oxide.

Instead of using iodine directly for the solution of the iron, a solution of iodine in iron iodide, as suggested by Eggertz,† may be used to great advantage, as it affords a ready method for getting rid of the impurities usually present in resublimed iodine. Treat 5 grammes of iron (as free as possible from silicon) with 25 grammes of iodine, and, when the solution is complete, add 30 grammes more of iodine, which will dissolve in the iron iodide in a few minutes. Dilute to 50 c.c. with cold boiled water and filter through a washed filter. Add the filtrate at once to 5 grammes of the weighed sample, and, after solution is complete, proceed as directed above.

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* Page 41.

† Jern-Kontorets Annaler, 1881, p. 301, and Chem. News, xliv. 173.

By Volatilization in a Current of Chlorine Gas.

Proceed exactly as in the method for the determination of silicon (pages 73 *et seq.*) until the boat is withdrawn from the combustion-tube. Wash the contents of the boat into a small beaker with a jet of cold water, and filter on a small ashless filter. The water dissolves any soluble metallic chlorides which are not volatile at a low red heat, and the insoluble matter in the filter consists of slag and carbon. Burn off the carbon and weigh the residue as Slag and Oxides. Or, if the carbon has been determined by another operation, filter the carbon and slag on a counterpoised filter * or on a Gooch crucible, dry at 100° C., and weigh as Carbon, Slag, and Oxides; by subtracting the weight of the carbon the difference is Slag and Oxides.

DETERMINATION OF PHOSPHORUS.

For the determination of phosphorus in iron and steel but two methods are in general use, either of which, properly carried out, will give extremely accurate results. Some chemists prefer one method, some the other, while a combination of the two is sometimes used. The two general methods are known respectively as the *Acetate Method* and the *Molybdate Method.* There are innumerable variations in the details, especially of the latter method, but any departure from what might be termed the standard instructions should never be attempted by any but a very experienced analyst.

The Acetate Method.

The essential parts of this method were suggested by Fresenius,† the changes and improvements in details being the work of many chemists.‡

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* See page 28.

† Jour. für Pr. Ch., xlv. 258.

‡ Tenth Census of the U. S., vol. xv. "Iron Ores of the U. S.," p. 523.

Treat 5 grammes of drillings in a No. 4 Griffin's beaker with 80 c.c. nitric acid (1.2 sp. gr.), and, when violent action has ceased, add 10 c.c. strong hydrochloric acid. Evaporate the solution to dryness in the air-bath, replace the cover, and heat until the ferric nitrate is nearly all decomposed. Cool, add 30 c.c. hydrochloric acid, heat gradually until the iron oxide is dissolved, and evaporate to dryness again in the air-bath. Cool, dissolve in 30 c.c hydrochloric acid, dilute, and, in steels or puddled iron, when silicon is to be determined, filter, and treat the insoluble matter as directed for the determination of silicon, on page 72.

In the case of pig-irons which may contain titanium, filter, and keep the residue of graphite, silica, etc., for treatment, as directed farther on, "when titanium is present."

In the case of steels, when silicon is not to be determined in this portion, the solution need not be filtered at all, but may be diluted at once to about 250 c.c.

In any case, heat the filtered or unfiltered hydrochloric acid solution nearly to boiling, remove the beaker from the light, and add gradually from a small beaker a mixture of 10 c.c. acid ammonium sulphite * and 20 c.c. ammonia, stirring constantly. The precipitate, which forms at first, redissolves, and when all but about 2 or 3 c.c. of the acid ammonium sulphite solution has been added, replace the beaker over the light. If at any time while adding the acid ammonium sulphite solution the precipitate formed will not redissolve even after vigorous stirring, add a few drops of hydrochloric acid, and, when the solution clears, continue the addition, very slowly, of the acid ammonium sulphite. After replacing the beaker on the light, add to the solution (which should smell quite strongly of sulphurous anhydride) ammonia, drop by drop, until the solution is quite decolorized, and until finally a *slight* greenish precipitate remains undissolved even after vigorous stirring. Now add the remaining 2 or 3 c.c. of the acid ammonium sulphite solution, which should throw down a white precipitate, which usually redissolves, leaving the solution quite clear and almost perfectly decolorized. Should any precipitate remain undissolved, however, add hydrochloric acid, drop by drop, until the solution clears, when it should smell perceptibly of sulphurous anhydride. If the reagents are used in exactly the proportions indicated, the reactions will take place as described, and the operations will be readily and quickly carried out. If the solution of acid ammonium sulphite is weaker than it should be, of course the ferric chloride will not be reduced, and the solution, at the end of the operation described above, will not be decolorized and will not smell of sulphurous anhydride. In this case add more acid ammonium sulphite (without the addition of ammonia) until the solution smells strongly of sulphurous anhydride, then add ammonia until the slight permanent precipitate appears, and redissolve it in as few drops of hydrochloric acid as possible. The solution being now very nearly neutral, the iron in the ferrous condition, and an excess of sulphurous acid present, add to the solution 5 c.c. of hydrochloric acid to make it decidedly acid and to insure the complete decomposition of any excess of the acid ammonium sulphite which may be present. Boil the solution,* while a stream of carbonic acid passes through it, until every trace of sulphurous anhydride is expelled, then pass a current of hydrogen suphide through it for about fifteen minutes to precipitate any arsenic which may be present, and finally allow the solution to stand in a warm place until the smell of hydrogen sulphide has disappeared, or, better, pass a current of carbonic acid through the solution, which will expel the hydrogen sulphide in a few minutes. The arrangement, Fig. 50, is convenient for this purpose. Filter from any arsenious sulphide, cuprous sulphide, sulphur, etc., into a No. 5 beaker, wash with cold water, and to the filtrate add a few drops of bromine-water, or of a solution of ferric chloride, and cool it by placing the beaker in cold water. To the cold solution add ammonia from a small beaker very slowly, and finally, drop by drop, with constant stirring. The green precipitate of ferrous hydrate which forms at first is dissolved by stirring, leaving the solution perfectly clear, but subsequently, although the green precipitate dissolves, a whitish one remains, and the next drop mmonia increases the whitish precipitate or gives it a reddish tint, and ly the greenish precipitate remains undissolved even after vigorous ing, and another drop of ammonia makes the whole precipitate appear n. If before this occurs the precipitate does not appear decidedly red olor, dissolve the green precipitate by a drop or two of hydrochloric

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* See page 44.

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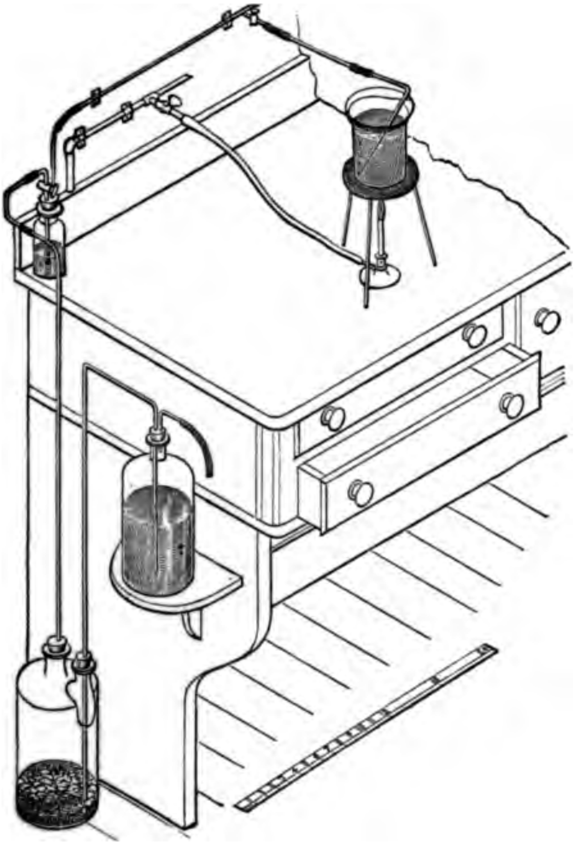
* By passing a current of carbonic acid through the boiling solution the sulphurous anhydride is soon expelled, and the operation requires no watching.

FIG. 50.



, and add a little bromine-water or ferric chloride solution (1 or 2 c.c.), add ammonia as before, and repeat this until the reddish precipitate btained, and then the green coloration as described above. Dissolve green precipitate in a very few drops of acetic acid (sp. gr. 1.04), n the precipitate remaining will be quite red in color, then add about

1 c.c. of acetic acid, and dilute the solution with boiling water, so that the beaker may be about four-fifths full. Heat to boiling, and when the solution has boiled one minute, lower the light, filter as rapidly as possible through a 5½-inch (140-mm.) filter, and wash once with hot water. The filtrate should run through clear, but in a few minutes it will appear cloudy by the precipitation of the ferric oxide, which has been formed by the exposure of the filtered solution to the air. The points to be observed are the red color of the precipitate and the clearness of the solution when it first runs through. Ferric phosphate being white, the red color of the precipitate shows that enough ferric salt was present in the solution to form ferric phosphate with all the phosphoric acid, and enough more to color the ferric phosphate red with the excess of ferric oxide.

When the precipitate has drained quite dry, pour about 15 c.c. of hydrochloric acid into the beaker in which the precipitation was made, warm it slightly so that the acid may condense on the sides and dissolve any adhering oxide, wash off the cover into the beaker, add about 10 c.c. of bromine-water, pour this on the filter containing the precipitate, allowing it to run around the edge of the filter, and let the solution run into a No. 1 Griffin's beaker. Wash out the beaker once or twice, and then wash the filter well with hot water. If the acid in the beaker is not sufficient to dissolve the precipitate completely, drop a little strong acid around the edge of the filter before washing it with hot water. The scaly film of difficultly soluble oxide which sometimes forms on boiling the acetate precipitate is caused by the presence of too much ammonium acetate, but when the instructions given above are carefully carried out it never appears. Evaporate the solution in the small beaker nearly to dryness to get rid of the excess of hydrochloric acid, add to it a filtered solution of 5 or 10 grammes of citric acid (according to the size of the precipitate of ferric oxide, etc.) dissolved in from 10 to 20 c.c. of water, then from 5 to 10 c.c. of magnesia-mixture and enough ammonia to make the solution faintly alkaline. Stand the beaker in cold water, and when the solution is perfectly cold, add to it one-half its volume of strong ammonia and stir it well. When the precipitate of ammonium-magnesium orthophosphate has begun to form, stop stirring, and allow it to stand in cold water for ten or fifteen minutes, then stir vigorously several times at intervals of a few minutes, and allow it to stand overnight. Filter on a small ashless filter, and wash with a mixture of 2 parts of water and 1 part of ammonia containing 2.5 grammes of ammonium nitrate to 100 c.c.

Dry the filter and precipitate, and ignite them at a very low temperature at first so as to carbonize the filter without decomposing the precipitate, which may then readily be broken up with a platinum wire. Raise the heat gradually, and finally ignite at the highest temperature of the Bunsen burner. When the precipitate is perfectly white, cool and weigh. Then fill the crucible half full of hot water, add from 5 to 20 drops of hydrochloric acid, and heat until the precipitate has dissolved. Filter off on another small, ashless filter any silica or ferric oxide that may remain, ignite, and weigh. The difference between the two weights is the weight of magnesium pyrophosphate, which, multiplied by 0.27836, gives the weight of phosphorus.

When Titanium is Present.

When a solution of ferric chloride containing titanic and phosphoric acids is evaporated to dryness, a compound of titanic acid, phosphoric acid, and ferric oxide is formed, completely insoluble in dilute hydrochloric acid.*

Iron ores and pig-irons containing titanic acid require, therefore, a somewhat different method of treatment from that given above.

Dry and ignite the residue of graphite, silica, etc., from the solution of the pig-iron, so as to burn off all the carbon. Moisten this residue with cold water, add from 5 to 10 drops of sulphuric acid and enough hydrofluoric acid to dissolve the silica, and evaporate until fumes of sulphuric anhydride are given off. While this is going on, proceed with the deoxidation of the filtrate as described above, but when the sulphurous acid has been driven off do not pass hydrogen sulphide through the solution, but cool it, and proceed with the acetate precipitation. Instead of dissolving the precipitate, after washing it as described above, dry the filter and precipitate in the funnel, being careful not to heat it so as to scorch the filter. Clean out any of the precipitate which may have adhered to the sides of the beaker in which the precipitation was made, by wiping it with filter-paper, and dry this paper with the filter and precipitate.

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* Published in Report on Methods employed in the Analysis of the "Iron Ores," Tenth Census U. S., xv. 512. I first noted this fact in 1878.

When the precipitate is quite dry, transfer to a small porcelain mortar. The precipitate may readily be detached from the filter by rubbing the sides of the latter together over a large piece of white, glazed paper, so that any little particles that fall out may be seen. Roll up the filter with the bits of paper which were used to wipe out the beaker, wrap a piece of platinum wire around it, burn it on the lid of the crucible in which the graphite residue was treated, and transfer the ash to the mortar. Grind the precipitate and ash with from 3 to 5 grammes of sodium carbonate and a little sodium nitrate, and transfer it to the crucible containing the residue which was treated by hydrofluoric and sulphuric acids. Clean the mortar and pestle by grinding a little more sodium carbonate, and add this to the other portion in the crucible. Fuse the whole for half an hour or more, cool, dissolve the fused mass in hot water, filter from the insoluble ferric oxide, etc.,* acidulate the filtrate with hydrochloric acid, add a few drops of acid ammonium sulphite, boil off all smell of sulphurous acid, and pass hydrogen sulphide through the hot solution to precipitate any arsenic that may be present. Pass a current of carbonic acid through the solution to expel the excess of hydrogen sulphide, filter off the arsenious sulphide, and to the filtrate add a sufficient amount of ferric chloride solution to combine with all the phosphoric acid as ferric phosphate and leave a slight excess. Add a slight excess of ammonia, which should throw down a red precipitate, while the solution is alkaline to test-paper; then add acetic acid to slightly acid reaction, boil, filter off the ferric phosphate and ferric oxide, and wash with hot water. Dissolve the precipitate in hydrochloric acid, allow the solution to run into a small beaker, evaporate until the solution is syrupy, add citric acid and magnesia-mixture, and precipitate the ammonium-magnesium orthophosphate as described above. Unless the amount of phosphorus is very small, a second fusion of the insoluble residue of ferric oxide, etc., is necessary. The two filtrates can then be added together, acidulated with hydrochloric acid, and the remainder of the process carried out as directed above. To avoid the fusion of the acetate precipitate with sodium carbonate, which is always troublesome, the method for the determination of phosphorus may be modified (in many cases with advantage, and generally when titanium is not to be estimated) as follows:

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* This ferric oxide, etc., contains all the titanium that was in the pig-iron as titanate of soda, and must be kept for the estimation of that element when it is to be determined.

After filtering off the insoluble matter,—graphite, silica, etc.,—ignite it, burn off the graphite, and treat the residue with hydrofluoric and sulphuric acids, evaporate down until the excess of sulphuric acid is driven off, and fuse with sodium carbonate. Treat the fused mass with water, and filter. Acidulate the filtrate with hydrochloric acid, and add it to the main solution, which has been deoxidized in the mean time with acid ammonium sulphite. Expel the last traces of sulphurous acid from the united filtrates by boiling and passing a current of carbonic acid through the solution, as previously directed. If the solution remains clear, pass hydrogen sulphide through it, and filter off the precipitated sulphides. Cool the solution, and make the acetate precipitation as directed on page 81. The only danger to be apprehended now is the tendency of titanic acid to separate out and carry phosphoric acid with it when in the evaporation of the hydrochloric acid solution of the acetate precipitate the liquid becomes concentrated. To avoid this, the evaporation must be watched very carefully, and citric acid added as soon as the titanic acid begins to separate. Then, if the separation has not proceeded too far, the phosphoric acid may be precipitated in the usual way. If, however, the separation of titanic acid is not checked in time, proceed with the evaporation as directed on page 84, add 5 c.c. strong hydrochloric acid, and warm gently. The solution will nearly always clear, but if it does not, add citric acid and a slight excess of ammonia, and filter. Stand the filtrate aside, burn off and fuse the precipitate with sodium carbonate, dissolve in water, filter, acidulate the filtrate with hydrochloric acid, add a little ferric chloride solution, a slight excess of ammonia, and acidulate with acetic acid. Boil, filter off the precipitate of ferric phosphate and oxide, dissolve in a little hydrochloric acid, allow the solution to run into a small beaker, evaporate down, and add it to the ammoniacal filtrate from the separated titanic acid obtained above. Add excess of magnesia-mixture, and precipitate the phosphoric acid in the usual way. When the solution becomes cloudy after deoxidation with acid ammonium sulphite, and remains so after acidulating with hydrochloric acid, proceed as directed above, but dry, and ignite the filter containing the precipitate by hydrogen sulphide and that on which the acetate precipitate was filtered, fuse with sodium carbonate, treat with water, filter, acidulate with hydrochloric acid, pass hydrogen sulphide through the solution, filter, add a little ferric chloride solution, and precipitate by ammonia and acetic acid. Add the solution of this precipitate, after filtering it off, to the solution of the main acetate precipitate, and proceed as before.

Instead of adding citric acid and magnesia-mixture to the solution of the acetate precipitate, Fresenius,* and afterwards Spiller,† advised the method of adding citric acid, excess of ammonia, and ammonium sulphide, filtering off the precipitated ferric sulphide, and, after evaporating to small bulk, adding magnesia-mixture and ammonia. When the bulk of the iron precipitate is not too great, this is quite unnecessary, for many determinations have shown that with an excess of magnesia-mixture, ammonium-magnesium orthophosphate is absolutely insoluble in both ferric-ammonium citrate and ammonium-aluminum citrate.

The precipitate is also insoluble in ammonia-water (1 part of ammonia to 2 parts of water).

The Molybdate Method.

Svanberg and Struve‡ first discovered the reaction on which this method is based, and Sonnenschein § first used it quantitatively. Dissolve 5 grammes of drillings in a No. 4 Griffin's beaker, in 80 c.c. nitric acid (1.2

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* Jour. für Pr. Chem., xlv. 258.

† Jour. Chem. Soc. (2), i.. 148.

‡ Jour. für Pr. Chem., xliv. 291.

§ Ibid., liii. 339.

p. gr.). Evaporate to dryness in the air-bath, replace the cover, and heat or one hour at a temperature of about 200° C. in order to decompose all he carbonaceous matter,* otherwise the precipitation of the phospho-molybdate will be incomplete. Allow the beaker to cool, dissolve the precipitate in 30 c.c. hydrochloric acid, evaporate to dryness to render the silica insoluble, redissolve in 30 c.c. hydrochloric acid, and evaporate carefully until the excess of hydrochloric acid is driven off. Add 30 c.c. nitric acid and evaporate nearly dry, add nitric acid again and evaporate to drive off all the hydrochloric acid, add from 50 to 100 c.c. molybdate solution,† heat it to 40° C. in a water-bath carefully kept at this temperature, and allow it to stand in the bath for about four hours. Filter on a small, washed filter, and wash thoroughly with dilute molybdate solution (1 part of solution to 1 part of water) until a drop of the filtrate gives no reaction for iron with potassium ferrocyanide. Stand the filtrate aside in a warm place to see whether any further precipitation of ammonium phospho-molybdate takes place; if it does, it must be filtered off and treated like the main precipitate. Pour 2 or 3 c.c. strong ammonia on the precipitate, stir it up with a fine jet of hot water, and allow the solution to run into the flask or beaker in which the precipitation of phospho-molybdate was made. When it has all run through the filter, replace the flask or beaker by a small beaker of a little over 100 c.c. capacity, remove any phospho-molybdate that may have adhered to the sides of the original flask or beaker, by means of the ammoniacal filtrate, and then pour this back on the filter and allow it to run through into the small beaker. Wash out the beaker or flask with hot water and pour it on the filter with the addition of a little more ammonia. Unless the precipitate of phospho-molybdate is very large, this amount of ammonia should dissolve it, and a very little more washing should be sufficient. If the precipitate is very arge, it may be necessary to use more ammonia and more wash-water, but nder all circumstances the amount of ammonia and of wash-water should e as small as is consistent with perfect solution of the precipitate and thorough washing of the beaker and filter. When the precipitate is small, the filtrate and washings should amount to about 25 c.c. Neutralize the solution with strong hydrochloric acid; if the yellow phospho-molybdate begins to precipitate, add ammonia until it redissolves, and if there should remain a flocculent white precipitate, probably silica, after the solution is quite alkaline, filter it off. Then to the cold alkaline liquid add, very slowly, 10 c.c. magnesia-mixture, stirring constantly, and after the magnesia-mixture is all in, add one-third the volume of the solution of strong ammonia and stir vigorously. It is well to stand the beaker in cold water and stir the solution several times after the precipitate has begun to crystallize out. After standing about four hours, it may be filtered off on a very small ashless filter and washed with dilute ammonia-water (1 part ammonia, 0.9 sp. gr., to 2 parts water) containing 2.5 grammes ammonium nitrate to the 100 c.c. Dry, ignite very carefully to burn off the carbonaceous matter, and finally heat for ten minutes over the blast-lamp to volatilize any molybdic acid that may have been precipitated with the ammonium-magnesium orthophosphate, cool, and weigh. Fill the crucible half full of hot water, add from 5 to 20 drops hydrochloric acid, and heat for a few minutes to dissolve the magnesium pyrophosphate. Pour the contents of the crucible on a small ashless filter, wash, ignite, and weigh the small residue that may remain undissolved. The difference between the two weights is the weight of magnesium pyrophosphate, which contains 27.836 per cent. phosphorus.

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* In 1877 I discovered the necessity for destroying the carbonaceous matter, and communicated he fact to Hunt and Peters, who mentioned it in the Metallurgical Review, ii. 365.

† See page 59.

Many chemists, following Eggertz,* prefer to weigh the yellow phospho-molybdate direct instead of dissolving it and precipitating as ammonium-magnesium orthophosphate. In this event take 1 gramme of the drillings and proceed exactly as directed above, but use only about one-third the amount of nitric and hydrochloric acids for the solution. Before adding the molybdate solution, the volume of the filtrate from the silica should amount to only about 25 c.c. Add 50 c.c. of the molybdate solution, allow it to stand four hours at a temperature of 40° C., and filter off the precipitated phospho-molybdate on a Gooch crucible; wash first with dilute molybdate solution, and finally with water containing 1 per cent. of nitric acid, dry in an air-bath heated to 120° C., and weigh as ammonium phospho-molybdate, containing 1.63 per cent. of phosphorus. In the absence of a Gooch crucible, use counterpoised filters * for weighing the phospho-molybdate. The points of special importance are:

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* Jour. für Pr. Chem., lxxix. 496.

First, the necessity for destroying all the carbonaceous matter by heating the nitric acid solution, after evaporation, to a sufficiently high temperature to effect this with certainty.

Second, the avoidance of the presence of hydrochloric acid in the final solution before precipitating by molybdate solution.

Third, when the phospho-molybdate is weighed directly, the necessity for rendering the silica insoluble.

Fourth, the danger of heating the solution above 40° C. after adding the molybdate solution, as arsenic, when present, precipitates with the phosphorus if the solution is heated to a higher temperature.

Fifth, the danger of causing a precipitation of molybdic acid with the phospho-molybdate by heating the solution to a temperature approximating 100° C.

The Combination Method.

Riley † was the first to suggest the precipitation of phosphorus as phospho-molybdate, preceded by a separation of the phosphoric acid from the mass of the ferric chloride by deoxidation and precipitation by the acetate method. This method was worked out afterwards by A. Wendel, of the Albany and Rensselaer Steel Company, S. Peters, of the Burden Iron Company, and J. L. Smith. ‡

Proceed as directed for the determination of phosphorus by the *Acetate Method*, using 1 gramme of borings and proportional amounts of reagents until having dissolved the acetate precipitate in hydrochloric acid, evaporate to dryness, redissolve in a very little nitric acid, dilute to 20 c.c. with water, add a slight excess of ammonia, redissolve the precipitated ferric oxide in nitric acid, and add 30 c.c. molybdate solution. Heat to 40° C. for an hour, filter, wash with water containing 1 per cent. of nitric acid, dry, and weigh.

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* See page 28.

† Jour. Chem. Soc., 1878, i. 104.

‡ Chem. News, xlv. 195.

When Titanium is Present.

When determining phosphorus in pig-irons containing titanium, burn off the residue of carbon, silica, etc., treat it with hydrofluoric and sulphuric acids, evaporate, and heat until the greater part of the sulphuric acid is driven off. Fuse with 2 or 3 grammes of sodium carbonate, dissolve in water, filter, acidulate the filtrate with nitric acid, add 50 c.c. molybdate solution, and heat to 40° C. for four hours. Filter, wash, and add this precipitate to the one obtained in the filtrate from the carbon, silica, etc. If any slight insoluble matter should remain on the filter upon dissolving in ammonia the phospho-molybdate obtained in the filtrate from the carbon, silica, etc., burn it, fuse it with sodium carbonate, and test it also for phosphorus.

The composition of the dried ammonium phospho-molybdate seems to vary very much, the percentage of phosphorus in it being given by various authorities from 1.27 to 1.75. It seems to depend upon various circumstances, such as the presence or absence of hydrochloric acid in the solution, the degree of acidity, the temperature at which the precipitation is effected, the length of time the solution stands before the precipitate is filtered off, the size of the precipitate, the state of concentration of the solution, and even the amounts of the iron and ammonium salts present.

This fact must be borne in mind when the phosphorus is determined by direct weighing of the phospho-molybdate, and every effort must be used to effect the precipitations always under as nearly as possible the same conditions.

RAPID METHODS.

Volumetric Method.*

Reduction by Zinc and Titration by Permanganate Solution.

This method gives an indirect determination of phosphorus by means of the estimation of the molybdic acid in the ammonium phospho-molybdate in which form the phosphorus is precipitated. The molybdic acid is reduced to a lower state of oxidation by the reducing action of zinc and sulphuric acid, and the reduced oxide is titrated with a standardized permanganate solution, molybdic acid being again formed by the reaction.

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* This method is the one prepared by the sub-committee on Methods of the International Steel Standards Committee of the United States. It is by far the best method known, and the results obtained by it are exceedingly accurate when the details are carefully observed. The sub-committee consists of W. P. Barba, A. A. Blair, T. M. Drown, C. B. Dudley (chairman), and P. W. Shimer.

FIG. 51.

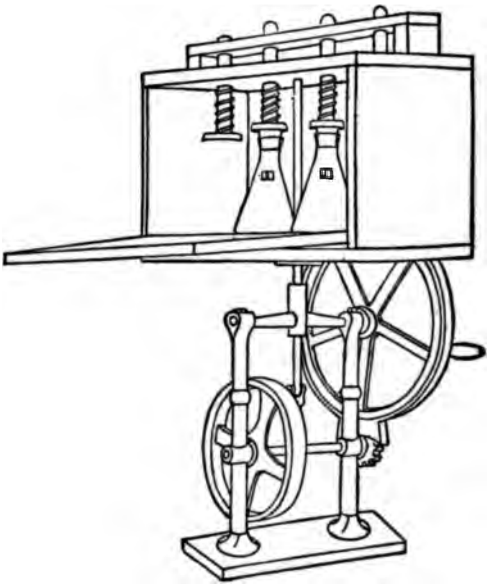


Fig. 51 shows a form of shaking-machine for shaking four flasks at once. The construction and method of use are apparent from the sketch.

Fig. 52 shows a form of reductor which is most convenient and efficient. The tube *a* is 0.018 m. inside diameter and 0.300 m. long. The small tube below the contraction with the stopcock *c* is 0.006 m. in inside diameter and 0.300 m. long below the stopcock. The tube is filled by placing at the point of contraction a flat piece of fine platinum gauze. On top of this is placed a plug of glass wool, about 8 mm. thick, and then asbestos, previously treated with concentrated hydrochloric acid, thoroughly washed, ignited, and diffused in water, is poured into the reductor tube until it forms a coating on top of the glass wool not over 1 mm. thick. This makes a filter which prevents very small pieces of zinc or other materials from being carried through. It is necessary to clean and refill the tube from time to time, as the filter after some use becomes clogged and the liquid passes too slowly. The tube is filled, as shown in the cut, with granulated amalgamated zinc. The reductor tube is fixed at such a height that when the block is removed from under the flask *f*, the latter may readily be detached from the tube and removed without disturbing the apparatus.

Fig. 53 shows the burette arranged for running the potassium permanganate directly into the flask, and needs no explanation. It should carefully calibrated.

FIG. 52.

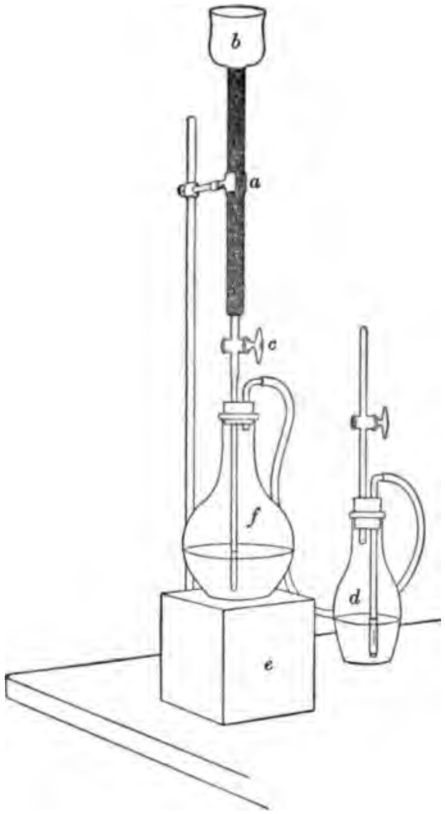
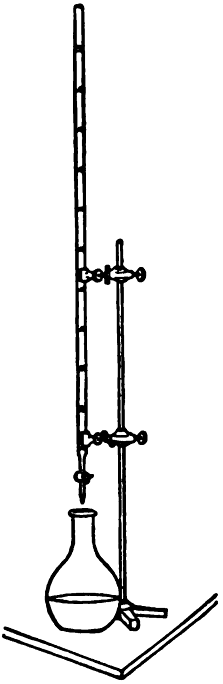


FIG. 53.



The various beakers, flasks, graduates, etc., required by this metl need no special comment.

Reagents.

Nitric Acid.—Nitric acid of 1.135 sp. gr., made by mixing C. P. ni acid (1.42 sp. gr.) with about three parts of distilled water.

Strong Sulphuric Acid.—The C. P. material of 1.84 sp. gr.

Dilute Sulphuric Acid.—Sulphuric acid 2½ per cent., by volume, made adding 25 c.c. of concentrated C. P. sulphuric acid to 1 litre of distilled wa

Strong Ammonia.—The C. P. material of 0.90 sp. gr.

Dilute Ammonia (0.96 sp. gr.).—Made by mixing concentrated C. P. ammonia-water of 0.90 sp. gr. with about one and a half times its volume of distilled water.

Strong Solution of Potassium Permanganate, for oxidizing the phosphorus and carbonaceous matter in the nitric acid solution of a steel. Made by dissolving from 12.5 to 15 grammes of crystallized potassium permanganate in 1 litre of distilled water and filtering through asbestos.

Standard Solution of Potassium Permanganate, for titrating the reduced solutions of ammonium phospho-molybdate. Made by dissolving 2 grammes of crystallized potassium permanganate in 1 litre of distilled water and filtering through asbestos. This solution is standardized as follows. Place from 0.15 to 0.25 gramme of thoroughly cleaned soft steel wire, in which the iron has been carefully determined, in each of three 125 c.c. Erlenmeyer flasks, and pour into each of the flasks 30 c.c. of distilled water and 10 c.c. of strong sulphuric acid. Cover with a small watch-glass and heat until solution is complete. Add a sufficient amount of the strong solution of potassium permanganate to oxidize the iron and destroy the carbonaceous matter, being careful to avoid an excess which would cause a precipitate of manganese dioxide. Should this occur, redissolve it by adding a very few drops of sulphurous acid and boil off every trace of the latter. Allow the solution in the flasks to cool and add to each 10 c.c. of dilute ammonia. Pass through the reductor and titrate in the flask.

In all cases the mode of procedure in using the reductor should be as follows. Everything being clean and in good order from previous treatment with dilute sulphuric acid, and washing with distilled water, and the flask being attached to the filter pump, pour 100 c.c. of warm dilute sulphuric acid into the funnel and open the stopcock *c*. When only a little remains in the funnel forming the top of the reduction tube, transfer the solution to be reduced to the funnel. This solution should be hot but not boiling. Pour some of the dilute sulphuric acid into the vessel which contained the solution to be reduced to wash it, and when only a little solution is left in the funnel as before, add this to the funnel in such a way as to wash it and follow with about 200 c.c. more of warm dilute sulphuric acid and finally with 50 c.c. of hot distilled water. In no case allow the funnel to get empty, and close the stopcock *c* when there is still a little of the wash-water left in the funnel above the surface of the zinc. This precaution prevents air from passing into the reductor tube. A blank determination is made by passing through the reductor a solution containing a mixture of 10 c.c. strong sulphuric acid, 10 c.c. dilute ammonia, and 50 c.c. water; preceded and followed by the dilute acid as described above. The amount of potassium permanganate required to give this blank a distinct color is subtracted from the amount required to give the same color to each reduced solution.

To get the value of the permanganate solution, multiply the weight of iron wire taken by the percentage of iron in the wire and divide by the number of cubic centimetres of potassium permanganate in terms of metallic iron. Multiply this result by 0.88163, the ratio of molybdic acid to iron, and the product by 0.01794, the ratio of phosphorus to molybdic acid, and the result is the value of 1 c.c. of the permanganate solution in terms of phosphorus. The ratio of molybdic acid to iron given above is that found when a known amount of molybdic acid in sulphuric acid solution is passed through the reductor in the manner described above and then titrated with potassium permanganate solution whose strength in terms of metallic iron is known. The reduction of the molybdic acid in the reductor in this case is to the form $Mo_{24}O_{37}$. The ratio of phosphorus to molybdic acid given above is that found by the analysis of the yellow precipitate of ammonium phospho-molybdate obtained from nitric acid solution of iron under varying conditions.

Sulphurous Acid.—A strong solution of the gas in water. Siphons of the liquefied gas may be obtained in the market.

Acid Ammonium Sulphite.—The strong C. P. solution of the reagent diluted with 10 parts of water.

Ferrous Sulphate.—Crystals of the salt free from phosphorus.

Sodium Thiosulphate.—Crystals of the salt free from phosphorus.

These four reagents are for reducing the excess of binoxide of manganese thrown down in oxidizing the carbonaceous matter in the nitric acid solutions of the steels. Any one may be used.

Molybdate Solution.—Place in a beaker 100 grammes of pure molybdic anhydride, mix it thoroughly with 400 c.c. cold distilled water and add 80 c.c. strong ammonia (0.90 sp. gr.). When solution is complete, filter and pour the filtered solution slowly and with constant stirring into a mixture of 400 c.c. strong nitric acid (1.42 sp. gr.) and 600 c.c. distilled water. Add 50 milligrammes of microcosmic salt dissolved in a little water, agitate thoroughly, allow the precipitate to settle for twenty-four hours, and filter before using.

Acid Ammonium Sulphate Solution, for washing the precipitate of ammonium phospho-molybdate. To 1 litre of water add 15 c.c. of strong ammonia (0.90 sp. gr.) and 25 c.c. strong sulphuric acid (1.84 sp. gr.).

Amalgamated Zinc.—Dissolve 5 grammes of mercury in 25 c.c. strong nitric acid diluted with an equal bulk of water, dilute to 250 c.c. and transfer to a stout flask of about 1000 c.c. capacity. Pour into it 500 grammes of granulated zinc which will pass through a 20-mesh sieve, but not through a 30-mesh. Shake it thoroughly for a minute or two and then pour off the solution, wash the zinc thoroughly with distilled water, dry, and preserve in a glass bottle for use.

Operation.

Weigh 2 grammes, or, in case of steels containing over 0.15 per cent. phosphorus, 1 gramme of the drillings and transfer them to a 250 c.c. Erlenmeyer flask, pour into the flask 100 c.c. of nitric acid (1.135 sp. gr.) and cover with a small watch-glass. Heat until the solution is complete and nitric oxide is boiled off. Add 10 c.c. of the strong potassium permanganate solution, boil until the pink color has disappeared and manganese dioxide separates. Continue the boiling for several minutes, then remove from the source of heat and add a few drops of sulphurous acid, a small crystal of ferrous sulphate, or a solution of 0.5 gramme of sodium hyposulphite in 10 c.c. of water, repeating the addition at short intervals until the precipitated manganese dioxide is dissolved. Boil two minutes longer, place the flask in a vessel of cold water, or allow it to stand in the air until it feels cool to the hand, and then pour in

40 c.c. of dilute ammonia (0.96 sp. gr.). The precipitated ferric hydrate will redissolve when the liquid is thoroughly mixed. When the solution is about the temperature of the hand, say 35° C., add 40 c.c. of molybdate solution at the ordinary temperature, close the flask with a rubber stopper, and shake it for five minutes, either by hand or in the machine, Fig. 51. Allow the precipitate to settle for a few minutes, filter on a 0.090 m. filter, and wash with acid ammonium sulphate solution until 2 or 3 c.c. of the wash-water give no reaction for molybdenum with a drop of ammonium sulphide. Pour 5 c.c. of ammonia (0.90 sp. gr.) and 20 c.c. of water into the flask to dissolve any adhering ammonium phospho-molybdate and then pour it on the precipitate in the filter, allowing the filtrate to run into a 250 c.c. Griffin's beaker. Wash out the flask and wash the filter with water until the solution measures about 60 c.c. Add to the liquid in the beaker 10 c.c. strong sulphuric acid and pass it through the reductor exactly in the manner described for the solution of ferric sulphate in standardizing the solution of potassium permanganate, being careful to keep the end of the small tube of the reductor just below the surface of the liquid in the flask. By adding the strong sulphuric acid to the ammoniacal solution immediately before passing it through the reductor it is heated sufficiently by the chemical action to insure thorough reduction. In washing be careful that no air passes into the reductor, and when the water has been drawn through, leaving a little still remaining in the funnel, close the stopcock, detach the flask F, wash off the drawn-out portion of the reductor tube into it, and titrate the solution with the standard permanganate. The reductor should be so arranged that the whole reduction occupies about three or four minutes. The solution that passes through should be bright green in color. In adding the permanganate, the green color disappears first, and the solution becomes brown, then pinkish yellow, and ultimately colorless. Continue the addition of the permanganate drop by drop, shaking the flask vigorously until the solution assumes a faint pink coloration, which remains after standing one minute. Subtract from the reading of the burette the amount given by a blank determination, obtained exactly as described under the method given above for standard-

izing the permanganate solution, multiply the number of c.c. so obtained by the value of 1 c.c. in terms of phosphorus, multiply by 100 and divide by the weight taken, and the result is the percentage of phosphorus in the steel.

When a large number of analyses are to be carried along at once the following modification is recommended. Obtain the yellow precipitate and dissolve in ammonia exactly as described above, except that the solution is allowed to run into the flask in which the precipitation was made, and the washing of the filter is continued until the solution amounts to 75 c.c. Add now to the flask 5 grammes of pulverized zinc, 100-mesh, pouring it into the flask through a funnel to prevent any zinc clinging to the sides of the flask. Then add to the flask 15 c.c. strong sulphuric acid (1.84 sp. gr.). This is most conveniently done in practice by letting it run in from a glass-stoppered burette. Close the flask at once with a rubber stopper carrying a glass tube bent twice at right angles, the farther arm dipping into a beaker containing a saturated solution of sodium bicarbonate. The flask should now stand undisturbed for about thirty minutes, when, if all action has ceased, it is ready to titrate with permanganate. The solution should be green, not brown. The temperature of the solution at the end of thirty minutes is about 40° C. and the titration succeeds best if done at this temperature. But the flask may stand a couple of hours without reoxidation of the reduced molybdic acid, and may then be successfully titrated. If the solution changes in color to brown the determination should be rejected, as the result will be too low. A blank should be made by adding to another flask 65 c.c. of water, 10 c.c. of dilute ammonia (0.96 sp. gr.), 5 grammes of the 100-mesh zinc, added in the manner described, and 15 c.c. of strong sulphuric acid (1.84 sp. gr.). This flask should be treated the same as the others and the amount of permanganate it uses up should be deducted from the amount required by each flask containing a test. When this method is used the reduction is practically complete to molybdic acid, so that the factor 0.85714 must be used instead of 0.88163.

Example.

0.1745 gramme of wire requires 50 c.c. of permanganate to give the required color. A blank determination gave 0.1 c.c., so that the wire actually required 49.9 c.c. permanganate. The wire contained 99.87 per cent. of iron, then 0.1745 × 0.9987 ÷ 49.9 equals 0.0034923, or 1 c.c. of permanganate equals 0.0034923 gramme metallic iron. Then multiplying the value in iron.by the ratio of molybdic acid to iron 0.88163 or 0.85714 and the product by the ratio of phosphorus to molybdic acid 0.01794, we have 0.0034923 × 0.88163 × 0.01794 equals 0.000055238, or 1 c.c. permanganate equals 0.000055238 gramme of phosphorus. Again, the precipitated ammonium phospho-molybdate from 2 grammes of steel required 35.6 c.c. permanganate less blank 0.1 c.c. equals 35.5 c.c.; 35.5 × 0.000055238 × 100 ÷ 2 equals 0.098 per cent. phosphorus.

Notes and Precautions.

It will be observed that the method given above oxidizes the phosphorus in the iron by means of nitric acid, completes and perfects this oxidation and possibly neutralizes the effect of the carbon present by means of potassium permanganate, and then separates the phosphoric acid from the iron by means of molybdic acid. The molybdic acid in the yellow phosphomolybdate is subsequently determined by means of potassium permanganate, the phosphorus being determined from its relation to the molybdic acid in this precipitate. The method given above applies to steel and wrought iron, but it is not yet recommended for pig-iron.

It is hardly necessary to say that all the chemicals and materials used in the analysis are assumed to be free from impurities that will injuriously affect the result.

1.135 sp. gr. nitric acid apparently oxidizes the phosphorus just as successfully as a stronger one, while by its use solution is sufficiently rapid, and there is less trouble during the subsequent filtration due to silica.

The boiling of the solution to remove nitrous acid and assist the action of the oxidizing permanganate seems to be essential. Some steels may not require 10 c.c. of the permanganate and some, like washed metal high in carbon, may require even more. It is essential that enough should be added to cause a precipitation of manganese dioxide and to give a strong pink color to the solution. This color gradually disappears on boiling. Less is required if the permanganate is added in small successive portions. Boiling two minutes after reducing the manganese dioxide removes any nitrous acid that may be formed by that operation.

In washing the yellow precipitate it shows some disposition to crawl up to the top of the filter. Care should therefore be taken to have the filter fit the funnel so closely that even if the precipitate does crawl over the top it will not be lost while washing the filter completely to the top. It is very easy to leave enough molybdic acid in the top of the filter, even though the washings are tested, to cause an error of .005 per cent. in the determination.

It is best to make up molybdate solution rather frequently. It is also best to keep it in the dark at a temperature not above 28° or 30° C. Much of the so-called molybdic acid of the market is ammonium molybdate or molybdate of some other alkali. This fact cannot be ignored in making up the molybdate solution. A series of experiments with various molybdic acids and alkaline molybdates obtained in the market indicates that if the amount of molybdic acid in the solution is that called for by the formula, irrespective of whether this amount is furnished by pure molybdic acid or by any of the commercial molybdates referred to, the result will be much nearer the truth than if this is not done. Good molybdic acid is the best, but the alkaline molybdates can be used. The amount of molybdic acid in these molybdates can readily be determined by dissolving 0.1000 gramme in 60 c.c. of water to which 10 c.c. of dilute ammonia have been added, filtering, adding 10 c.c. strong C. P. sulphuric acid, and passing through the reductor as above described. The method given in the example above enables the amount of molybdic acid to be determined. If the molybdic acid as obtained in the market, or the ammonia used in dissolving it, contains any soluble silicates, the resulting molybdate solution will be yellowish in color and the determination made with this solution will be high, owing apparently to ammonium silico-molybdate being dragged down with the phospho-molybdate. Treatment of the molybdate solution with microcosmic salt, as described, overcomes this difficulty and gives a perfectly colorless molybdate solution. A molybdate solution tinged with yellow should never be used. It will be observed that the molybdate solution recommended above contains much less ammonium nitrate than is given by many of the formulas now in use. Experience shows that a molybdate solution made on this formula keeps much better than those containing more ammonium nitrate. It will also be observed that the amount used for each determination is less than many methods employ. It is believed that the amount recommended is sufficient and that the ammonium nitrate required to assist the formation of the yellow precipitate is furnished by the 40 c.c. of dilute ammonia added to the nitric acid solution of the steel. Of course the molybdate solution recommended above cannot be used for other work interchangeably with that made on the older formulas, on account of lack of ammonium nitrate.

The directions in regard to the reductor, both as to making and use, should be strictly followed. By the use of the stopcock and the amalgamated zinc, and by keeping a little liquid in the funnel, the same blank can be obtained from a reductor almost continuously, even though two or three days of standing intervene between blanks. It is, however, always advisable to treat with dilute sulphuric acid and wash before using, even though only one night has elapsed since the last previous use. If the solution to be reduced does not contain enough acid or is not warm enough, the reduction will not be complete. Care should therefore be taken not to allow too much mixing of the dilute sulphuric acid with the solution to be reduced, either in the funnel or in the reductor tube itself. The best asbestos to use is the mineral known as actinolite, but any fibrous mineral which will act as a filter and not be dissolved by the acids used may be employed. Glass wool alone will not do, as a good filter is essential in order that neither small particles of zinc nor impurities in the zinc may be drawn down into the flask with the reduced solution. The consumption of zinc is very small.

In testing with ammonium sulphide, to see whether the washing of the yellow precipitate is complete, good results are obtained by putting two or three drops of yellow ammonium sulphide into a few cubic centimetres of distilled water, and allowing the washings to drop into this solution from the stem of the funnel. If iron is present in the washings it will show while the solution is still alkaline. By allowing the washings to continue running into the ammonium sulphide solution it soon becomes acid, when molybdenum, if any is present, shows by a more or less brownish color. If the acid solution is pure white from separated sulphur the washing is complete.

Since the acidity of the solution in which the yellow precipitate is formed has an influence on its composition, it is quite desirable that the sp. gr. of the 1.135 nitric acid and of the 0.96 ammonia should be taken with some care. The temperature at which the figures are correct is 15° C. It is best to use the Westphal balance in determining these gravities, but, failing this, a sufficiently delicate hydrometer may be employed.

In using the reduction with 5 grammes of 100-mesh zinc, it will be observed that as the zinc becomes nearly all dissolved a blackish residue remains. This residue seems to be metallic lead. It disappears slowly during the titration and apparently uses up some permanganate. It takes a little longer to secure a satisfactory end reaction with the 100-mesh zinc, as the pink color fades out several times before it will remain permanent for one minute. It is essential that air should be excluded from the flask after the reduction is nearly complete, and it is for this purpose that the sodium bicarbonate solution is used. A tendency to suck the soda solution back into the reducing flask will be noticed, due to the cooling of the flask. The reduction should be made in a place free from draughts.

With the amalgamated zinc in the reductor made as above described the blank generally uses up about 0.1 c.c. of the standard permanganate solution. The blank when using the reduction by means of 5 grammes 100-mesh zinc usually amounts to 0.6 c.c. of the standard permanganate, and may be higher. Pulverized zinc is rarely free from sulphides, and while this seems not to be a very important matter, it is nevertheless not recommended to use, either in the reductor or in the flask reduction, a zinc that gives a high blank.

If the amount of sulphurous acid or other reagent added to the nitr acid solution to remove the precipitated binoxide of manganese is insuff cient, a brown stain will be left on the filter-paper after the yellow precip tate is dissolved in ammonia. This may occur even though the nitric aci solution looks clear, and as no harm can arise from a slight excess of th reducing agent, it is usually more satisfactory to add an excess. It is nc desirable to add the reducing agent to the solution while boiling, as unde such circumstances it frequently boils over.

It is rather essential to use the dilute sulphuric acid warm, so that th general temperature of the reductor may be kept up.

A good method for cleaning the wire in standardizing the potassiur permanganate is as follows. Take a round lead-pencil and make a hol in it with a pin near the end. Insert the end of the wire in this hole an revolve the pencil until there are two turns of the wire around it. Hol the turns firmly in one hand and cut the wire so that about 0.75 m. wi remain attached to the pencil. Draw this wire through a piece of folde fine sand-paper several times and then several times through a piece c filter-paper. Seize the wire near the pencil with the filter-paper and cut o the part which was wound around the pencil and remove it. Then inse the end of the cleaned wire in the hole and revolve the pencil with or hand, holding the wire in the filter-paper in the other hand, until it is a wound loosely on the pencil. Push the coiled wire off the end of tl pencil. It is now in a convenient form for weighing.

Alkalimetric Method.[*]

The principle on which this method is based is the acidity of ammoniu phospho-molybdate, which, according to the following reaction, requires : molecules of alkali for its neutralization.

$$2[(NH_4)_3 12MoO_3,PO_4] + 46NaHO + H_2O = 2\,[(NH_4)_2HPO_4] + (NH_4)_2 MoO_4 + 23Na_2MoO_4 + 23H_2O.$$

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[*] This method was introduced by Mr. James O. Handy, of Pittsburg, to whose work ma of the details are due. It is quite extensively used and is extremely rapid. Mr. Handy kin prepared the essential part of this description.

Reagents.

Molybdate Solution.—The solution described in the last method (page 97) may be used.

Nitric Acid for Washing Precipitates.—A 1 per cent. solution of nitric acid: add 13 c.c. of strong nitric acid (1.42 sp. gr.) to 1 litre of water.

Potassium Nitrate Solution.—A 1 per cent. solution of potassium nitrate: dissolve 1 gramme of potassium nitrate in 1 litre of water.

Phenolphthalein Solution.—A 0.2 per cent. solution of phenolphthalein: dissolve 1 gramme of phenolphthalein in 500 c.c. of 95 per cent. alcohol.

Standard Solution of Sodium Hydroxide.—To 100 grammes pure sodium hydroxide add an amount of water just insufficient to completely dissolve it. Pour it into a tall cylinder, close the cylinder and allow the insoluble matter, sodium carbonate, etc., to settle. The clear liquid will be practically free from carbonate. Dilute it in the proportion of 30 c.c. to 2 litres of water.

Standard Nitric Acid.—Measure 2 litres of water into a glass-stoppered bottle, add 20 c.c. of nitric acid (1.42 sp. gr.) and mix thoroughly. Measure accurately 10 c.c. of the "Standard Solution of Sodium Hydroxide." Place them in a small flask, add 40 c.c. of water and 3 drops of "Phenolphthalein Solution." Drop "Standard Nitric Acid" from a carefully calibrated burette into the flask until the pink color just disappears. If the solutions are not of the same strength, dilute the stronger with water until they agree. For example, if it required 9.5 c.c. of nitric acid to discharge the color, return the nitric acid from the burette to the bottle and dilute it according to the following proportion: 9.5 : 10 = 2030 (the volume of nitric acid remaining) : 2136.9.

Add 106.9 c.c. of water to the nitric acid, and after thoroughly mixing it retest as above.

If it should require 10.5 c.c. of the nitric acid solution to discharge the color, dilute the sodium hydroxide solution according to the proportion: 10 : 10.5 = 2010 (the volume of sodium hydroxide remaining) : 2110.5.

Add 100.5 c.c. of water to the solution of sodium hydroxide, mix thoroughly, and retest.

The standard solutions being equal in strength, standardize them follows:

Titrate the ammonium phospho-molybdate obtained from a steel which the phosphorus has been carefully determined, and divide the pe centage of phosphorus by the number of c.c. of the "Standard Solution c Sodium Hydroxide" required to neutralize it. The result is the value c the "Standard Solution of Sodium Hydroxide." *

Operation.

Precipitate the ammonium phospho-molybdate from 2 grammes of th steel exactly as described in the last method "Reduction by Zinc an Titration by Permanganate Solution."

Filter and wash first with "Nitric Acid for Washing Precipitates" an then with "Potassium Nitrate Solution" until the washings are no long acid. Place the filter and precipitate in the flask in which the precipitatic was made and run in from a pipette 10 c.c. of the "Standard Solution Sodium Hydroxide." If, after agitation, this is insufficient to dissolve tl precipitate, add 10 c.c. more, and if necessary continue the additions unt the precipitate is dissolved. Dilute to 50 c.c., add 3 drops "Pheno phthalein Solution," and add from a burette "Standard Nitric Acid" unt the pink color disappears. Subtract the number of c.c. of "Standa Nitric Acid" used from the number of c.c. of "Standard Solution Sodium Hydroxide" taken to dissolve the precipitate, and the remaind will be the number of c.c. of the "Standard Solution of Sodium Hydro ide" required to neutralize the ammonium phospho-molybdate. Fro this calculate the amount of phosphorus in the steel.

Direct Weighing of the Phospho-Molybdate.

Instead of using the volumetric method, some chemists prefer weigh the yellow precipitate. Mr. Wood's method † is as follows:

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* Mr. Handy prefers to have the solutions of such strength that 1 c.c. = 0.0002 gramme ph phorus. To obtain this result calculate the weight of phosphorus to which each c.c. of the solutio is equivalent and dilute them as required.

† Communicated to the author. Mr. Wood states that the details adapting this to a "rap method" were worked out by Mr. J. A. Nichols, of the Homestead Works.

Dissolve 1.63 grammes steel in a six-ounce Erlenmeyer flask in 30 c.c. warm nitric acid (1.2 sp. gr.), place the flask over a Bunsen flame and evaporate down to 10 or 15 c.c., hastening the evaporation by blowing a gentle current of air into the flask.

Heat 50 c.c. of molybdate solution to 50° or 55° C., add it to the solution in the flask, and shake well. Complete precipitation should take place in from three to five minutes. Filter on the pump in a 7 cm. Munktell's No. 1 filter which has previously been washed, dried at 100° C., and weighed. Wash with dilute nitric acid, suck dry, wash once with alcohol and thoroughly with ether, and place the filter containing the precipitate in a funnel in an air-bath heated to 110° C. The funnel in the bath is connected with the exhaust so that the precipitate and filter are thoroughly dried in from one to three minutes, according to the size of the precipitate. Weigh, and 1 milligramme of the precipitate will be equal to .001 per cent. of phosphorus in the steel.

In the case of pig-iron and spiegel, the metal, after solution in nitric acid (1.2 sp. gr.), is diluted with 20 c.c. water, 5 drops of hydrofluoric acid are then added, the solution is boiled for two or three minutes, filtered through asbestos on the pump, and concentrated to 15 c.c.

15 c.c. of chromic acid are added, the solution is boiled down again and precipitated as above. The hydrofluoric acid prevents the separation of gelatinous silica, but does not interfere with the precipitation of phosphorus.

This method will not work with ferro-manganese, as the combined carbon is not sufficiently oxidized and prevents the precipitation of all the phosphorus.

The solutions referred to above are prepared as follows:

Molybdic acid solution. To 1200 c.c. water add 700 c.c. ammonia (sp. gr. 0.88) and one pound molybdic acid; when the molybdic acid is dissolved add 300 c.c. nitric acid (sp. gr. 1.42), and cool. Pour this solution into a mixture of 4800 c.c. water and 2000 c.c. concentrated nitric acid. Filter for use after standing twenty-four hours.

Chromic acid solution: 1.42 sp. gr. nitric acid saturated with chromic acid.

DETERMINATION OF MANGANESE.

The Acetate Method.

Dissolve 1 gramme of drillings in 15 c.c. nitric acid (1.2 sp. gr.) in a No. 2 Griffin's beaker. Evaporate to dryness in the air-bath, and heat to decompose carbonaceous matter. Allow the beaker to cool, add 10 c.c. hydrochloric acid, heat carefully until all the ferric oxide is dissolved, evaporate to dryness to get rid of all the nitric acid, redissolve in 10 c.c. hydrochloric acid, and evaporate carefully until the solution is almost syrupy. Dilute with cold water to about 100 c.c., and filter off the insoluble matter, allowing the filtrate and washings to run into a No. 6 Griffin's beaker. In the case of steel or puddled iron the filtration may be omitted, the solution being poured into the large beaker, and the rinsings of the small beaker added. To the solution in the large beaker, which should amount to about 200 c.c., add a solution of sodium carbonate very slowly, stirring vigorously. The solution will finally become very dark red in color, and the precipitate formed will redissolve very slowly. Add the solution of sodium carbonate 2 or 3 drops at a time, stir well, and allow the solution to stand several minutes, to see whether or not the precipitate will redissolve. When, under these circumstances, a decided precipitate remains, add 2 drops of hydrochloric acid, stir well, and allow the solution to stand for some minutes; if the solution does not clear, add 2 drops more, and stir again. If the first part of the operation has been carefully conducted, this amount of hydrochloric acid will usually be sufficient, but if, for any reason, too large a precipitate has been formed, it may require a few drops more. It is important, however, that no more hydrochloric acid be added than just enough to redissolve the precipitate formed by the sodium carbonate, and, to insure this, the solution should be well stirred and allowed to stand a sufficient length of time after each addition of hydrochloric acid. The solution may be so dark in color that it is difficult to see when the precipitate does finally disappear, but by tanding the beaker on a piece of white paper the light reflected hrough the bottom of the beaker will greatly diminish the difficulty. When, under this method of procedure, the solution clears, add 2 grammes of sodium acetate dissolved in a few c.c. of water, stir well, and dilute the solution to about 700 c.c. with boiling water. Heat it to boiling, and allow it to boil for about ten minutes, then remove it from the tripod, and allow the precipitated ferric hydrate and acetate to settle. Decant the clear, supernatant fluid on a large washed filter, throw the precipitate on, and wash it two or three times with boiling water, allowing the filtrate to run into a large beaker or flask, from which it can be transferred to a platinum or porcelain dish and evaporated rapidly. When the precipitate has drained quite dry, by means of a platinum spatula transfer it to the beaker in which the precipitation was first made; dissolve the precipitate which remains adhering to the filter, and that which remains on the blade of the spatula, by pouring around the edge of the filter and on the spatula held over it 10 c.c. hydrochloric acid diluted with twice its volume of hot water, and heat the beaker containing the precipitate. Wash the filter free from ferric chloride with cold water, and heat the beaker containing the precipitate until the latter is dissolved. Cool the solution, and repeat the precipitation, filtration, and resolution of the precipitate precisely as in the first case, adding this filtrate to the first one. Precipitate, filter, and wash a third time in the same manner, evaporate all the filtrates together until they are reduced to about 300 c.c. in volume, and transfer this solution to a No. 3 beaker.

If during the evaporation any manganese has become oxidized by exposure to the air, it forms a hard ring on the side of the capsule, and may be dissolved, after the solution is poured into the beaker, by two or three drops of hydrochloric acid, and washed into the beaker. Should any ferric oxide separate out, pour the solution in the capsule through a small filter, allowing it to run into the beaker, wash the precipitate with hot water, dissolve it in a very few drops of dilute hydrochloric acid, and let it run into a No. 1 beaker. Add just enough solution of sodium carbonate to precipitate it, make it faintly acid with acetic acid, boil it, and filter into the main solution.

This solution now contains all the manganese, nickel, and cobalt and the greater part of the copper which may have been in the metal. Add to it 10 grammes of sodium acetate and a few drops of acetic acid, heat it to boiling, and pass a current of hydrogen sulphide through the boiling solution for fifteen minutes. This will precipitate the copper, cobalt, and nickel. Filter off the black sulphides, boil the filtrate to expel the excess of hydrogen sulphide, let the solution cool somewhat, and add bromine-water in excess. If no precipitate forms at first, stand the solution, which should be colored by the bromine-water, in a warm place for an hour or two, to allow the precipitate of manganese dioxide to separate out. If a precipitate forms immediately, add bromine-water until, when the precipitate settles, the solution is strongly colored by it, and stand it aside for an hour or two. At the end of this time, the precipitate having settled and the supernatant fluid being still colored by the bromine, heat it carefully, finally to boiling, and expel the excess of bromine; allow the precipitate to settle, filter, wash very carefully, and avoid stirring up the precipitate when it is on the filter, as it has a tendency to go through. Dissolve the precipitate on the filter in sulphurous acid water containing a little hydrochloric acid; allow the solution to run into a platinum dish, and wash the filter well. A little of the sulphurous acid water will quickly dissolve any manganese dioxide which may adhere to the beaker in which it was precipitated, and this may be poured on the filter. Boil the solution in the dish to expel the excess of sulphurous acid, add from 5 to 20 c.c. of a clear filtered solution of microcosmic salt, heat to boiling, and add ammonia, drop by drop, with constant stirring. When the precipitate of ammonium-manganese phosphate begins to form, stop adding ammonia, and stir until the precipitate becomes crystalline. When this change occurs, add one more drop of ammonia; the additional precipitate formed will be curdy, but a few seconds' continued stirring at the boiling temperature will change it to the silky crystalline condition. Continue the addition of ammonia in exactly the same manner until the precipitate is all down and further additions of ammonia fail to change the silky appearance. Add a dozen drops of ammonia in excess, remove the dish from the light, and stand it in ice-water until perfectly cold. Filter on an ashless filter, wash with cold water containing 10 grammes of ammonium nitrate (dissolved in water made faintly alkaline with ammonia and filtered) in 100 c.c. until the filtrate gives no reaction for hydrochloric acid, dry, ignite, and weigh as manganese pyrophosphate, which contains 38.74 per cent. manganese. During the precipitation of the ammonium-manganese phosphate the stirring must not be discontinued for an instant, as the solution has a great tendency to bump when the precipitate is allowed to settle. The crystalline condition of the precipitate, which is absolutely necessary for the success of the determination, can most readily be brought about by the means described above. It can, of course, be accomplished by adding an excess of ammonia at once, but it will require much more boiling and stirring than the method above described. The final precipitation as ammonium-manganese phosphate, due to Dr. Gibbs, is much the most accurate method known. A common practice, however, is to wash the bromine precipitate of hydrated manganese dioxide, dry, ignite, and weigh as manganoso-manganic oxide, which contains 72.05 per cent. manganese. There are two objections to this method of procedure: first, the difficulty of washing the manganese dioxide free from sodium salts; secondly, the uncertainty as to the exact state of oxidation of the ignited manganese oxide.

The first of these objections Eggertz claims to overcome by washing the precipitated manganese with water containing 1 per cent. of hydrochloric acid. It may also be overcome, or rather the danger may be avoided, by using no fixed alkalies. By this method, nearly neutralize the hydrochloric acid solution of the iron or steel by ammonia, then add a solution of ammonium carbonate exactly as directed above for sodium carbonate, and finally, instead of sodium acetate, add ammonium acetate (5 c.c. of ammonia slightly acidulated by acetic acid). Evaporate the filtrates obtained in this way to about 500 c.c., transfer to a flask of about 1 litre capacity, and cool. When perfectly *cold*, add 3 or 4 c.c. bromine, shake well, and when the solution is strongly colored all through by bromine, add an excess of ammonia, and heat to boiling. Filter, wash with hot water, dry, ignite, and weigh as manganoso-manganic oxide.

The second objection seems, according to Pickering,[*] to be well founded, the amount of manganese in the ignited oxides varying from 69.688 per cent. to 74.997 per cent., according to the temperature to which they were heated and other undetermined conditions. This cause of error may be avoided by weighing the precipitate as manganous sulphide, containing 63.18 per cent. manganese. This method, due to H. Rose,[†] is carried out as follows. Ignite the oxide in a porcelain crucible, allow it to cool, mix it with five or six times its volume of flowers of sulphur, place the crucible on a triangle, and insert the bowl of a clay tobacco-pipe, which should be large enough to quite fill the top of the crucible and too large to reach to the precipitate. Pass through the stem a current of dry hydrogen until all air is expelled, heat the crucible gradually to as high a heat as a good Bunsen burner will produce, cool in the current of hydrogen, and weigh as manganous sulphide.

General Remarks on the Acetate Method.

The chief source of error in the acetate method, as it is usually practised, is in the addition of too much sodium acetate, whereby the manganous chloride is changed to manganous acetate, which, according to Kessler,[‡] is readily decomposed to manganous oxide and acetic acid. Under these circumstances, a larger amount of manganese is precipitated with the iron than would be the case if a less amount of sodium acetate were added. When sodium acetate is added to ferric chloride, the reaction may be written, $6NaC_2H_3O_2,3H_2O + Fe_2Cl_6 = 6NaCl + Fe_2(C_2H_3O_2)_6 + 3H_2O$; and to precipitate the iron as ferric acetate in 1 gramme of metal would necessitate the use of 8 grammes of sodium acetate. But, as Kessler in the same article remarks, when a solution of ferric chloride is treated with sodium carbonate and hydrochloric acid exactly as described above, a liquid is formed which contains fourteen times its equivalent of *ferric hydrate* in solution. Consequently ½ gramme of sodium acetate would be sufficient to precipitate 1 gramme of iron as ferric hydrate and basic acetate. In order, however, to precipitate the manganese as manganese dioxide by bromine, it is necessary to convert all the manganous chloride into manganous acetate: consequently an excess of sodium acetate is added before adding bromine. If, when making the acetate precipitation, the solution contains any ferrous chloride, a "brick-dust" precipitate is usually formed, which generally passes through the filter, and is very difficult to dissolve or manage in any way. It is usually the shortest and best plan, in this event, to start a fresh portion and throw away the other.

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[*] Chem. News, xliii. 226.

[†] Rose, Quant. Anal. (French ed.), p. 104.

[‡] Chem. News, xxvii. 14.

The Nitric Acid and Potassium Chlorate Method.

(*Ford's Method.*)

The acetate method is at best very tedious, and when the amount of manganese is very small it is of course desirable to work on larger amounts than 1 gramme of the sample, but in this event the iron precipitate is so large that it becomes very difficult to manage it properly. With Ford's method however, there is almost no limit to the amount which can be operated upon, and many experiments have shown that with proper precautions it is an extremely accurate process. The reaction on which the process is based was first noticed by Hannay * in 1878; but Ford † first worked out the method in its present practical form. Dissolve 5 grammes of borings in a No. 3 beaker in 60 c.c. nitric acid (1.2 sp. gr.), evaporate down until the solution is almost syrupy, then add 100 c.c. strong nitric acid (1.4 sp. gr.) and 5 grammes potassium chlorate. Heat the solution to boiling either on the hot plate or on a tripod with a thin piece of sheet asbestos, about 1 inch (25 mm.) in diameter, on the centre of the wire gauze. Boil the solution fifteen minutes, remove the light, add 50 c.c. strong nitric acid and 5 grammes potassium chlorate, replace the light, and boil fifteen minutes longer, or until the yellowish fumes from the decomposition of the potassium chlorate are no longer given off. Cool the solution as rapidly as possible by standing the beaker in cold water, filter on the pump, using the cone ‡ or glass filtering-tube with asbestos filter,* and wash two or three times with strong nitric aci which must be free from nitrous fumes.† Nitrous acid reduces manganes dioxide to manganous oxide, which then dissolves in nitric acid. It presence may be recognized by the yellow color it imparts to nitric acid and it may be removed by blowing air through the acid. It is alway formed in nitric acid which has been exposed to sunlight, and for that reason this acid should be kept in a dark place. Suck the precipitate dry, and transfer it, with the asbestos filter, to the beaker in which the precipitation was made. Pour into the beaker from 10 to 40 c.c. strong sulphurous acid water, which will dissolve the precipitate almost instantly. By pouring it through the cone or filtering-tube, any adhering precipitate will be dissolved and carried into the beaker. As soon as the precipitate is dissolved, filter from the asbestos into a No. 1 beaker, washing with hot water, and add to the filtrate from 2 to 5 c.c. hydrochloric acid. Heat the filtrate until the excess of sulphurous acid is driven off, add bromine-water until the solution is strongly colored with it, and boil off the excess of bromine. Add ammonia until the solution smells quite strongly of it, boil for a few minutes, and filter into a No. 3 beaker. Wash several times with hot water, remove the beaker, dissolve the ferric hydrate on the filter in dilute hot hydrochloric acid (1 part of acid to 3 of water), allowing the solution to run back into the beaker in which the precipitation was made, and wash the filter with hot water. Boil this filtrate for a few minutes to drive off the chlorine which may be present from the solution of any little manganese dioxide precipitated with the ferric hydrate, reprecipitate by ammonia as before, filter, and repeat the solution, precipitation, and filtration, allowing all the filtrates from the ferric hydrate to run into the No. 3 beaker. Acidulate this solution, which will be about 300 or 400 c.c. in volume, with acetic acid, heat to boiling, and pass hydrogen sulphide through the boiling solution for ten or fifteen minutes. Filter into a platinum dish from any cobalt sulphide, which is the only metal likely to be present with the manganese; boil off the hydrogen sulphide after adding a little hydrochloric acid, add microcosmic salt, and precipitate, filter, ignite, and weigh, as directed on pages 110 and 111, as manganese pyrophosphate.

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* Jour. Chem. Soc., xxxiii. 269.

† Trans. Inst. Min. Engineers, ix. 397.

‡ See page 27.

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* As described under Methods for Determination of Carbon.

† It is always well to transfer the filtrate and washings to a No. 4 beaker, add 2 grammes potassium chlorate, and boil again, to see whether any further precipitate of manganese dioxide is formed.

Steels containing much Silicon.

In steel high in silicon (0.2 per cent. and over) the gelatinous silica formed is very apt to clog the filter when operating as described above, and it is better to dissolve the sample in hydrochloric acid, evaporate to dryness, being careful not to heat it too hot, redissolve carefully in 50 c.c. strong nitric acid, boil down until nearly syrupy to destroy all the hydrochloric acid, redissolve in 100 c.c. strong nitric acid, and precipitate as directed above.

Instead of dissolving in hydrochloric acid, Mr. Wood suggests adding a few drops of hydrofluoric acid to the nitric acid solution before evaporating. This seems to work extremely well, and saves much time in the case of high silicon steels. It may also be used to advantage in the case of pig-iron instead of the method given below.

Pig-Iron.

Dissolve 5 grammes in 50 c.c. dilute hydrochloric acid (1 part hydrochloric acid to 1 part water), filter on a washed filter into a No. 3 beaker, evaporate to dryness, redissolve in 50 c.c. strong nitric acid, and proceed as in the case of "steel high in silicon."

Spiegel and Ferro-manganese.

It is best to use only 1 gramme of spiegel or ferro-manganese of from 20 to 40 per cent. manganese and .5 gramme or $\frac{1}{10}$-factor weight of very high (from 60 to 80 per cent.) ferro-manganese. In the latter, indeed, it is better to use the acetate method with ammonia and acetic acid, and, omitting the precipitation by bromine, boil off the hydrogen sulphide from the filtrate from the insoluble sulphides, after adding hydrochloric acid, and then precipitate by microcosmic salt as directed above.

RAPID METHODS.

Volumetric Methods.

Volhard's Method.[*]

This method is based on the principle announced by Morawski and Stingl,[†] that when potassium permanganate is added to a neutral manganous salt all the manganese is precipitated, in accordance with the reaction $4KMnO_4 + 6MnSO_4 + 4H_2O = 10MnO_2 + 4KHSO_4 + 2H_2SO_4$. When all the manganous salt is oxidized, the solution is colored by the permanganate, which thus indicates the end reaction. The permanganate used for titrating iron ores may be used for this determination, and, its value being determined, as directed, in terms of iron, the calculation for manganese is as follows. The reaction, when permanganate is added to a solution of ferrous sulphate, is $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$, or 2 molecules of potassium permanganate oxidize 10 molecules of ferrous sulphate. Now, as 2 molecules of permanganate oxidize 3 molecules of manganous sulphate, while 2 molecules of permanganate oxidize 10 molecules of ferrous sulphate, the oxidizing power of the permanganate is only three-tenths as great in the former case as it is in the latter, and its value in manganese is to its value in iron as 3 is to 10, or $\frac{55}{56} \times \frac{3}{10} = \frac{165}{560}$. Therefore the value of the permanganate in iron multiplied by $\frac{165}{560}$ or $0.2946 =$ its value in manganese.

Dissolve 1.5 grammes of borings in a platinum or porcelain dish in 25 c.c. nitric acid (1.2 sp. gr.). When solution is complete, add 12 c.c. dilute sulphuric acid (1 part concentrated sulphuric acid and 1 part water), and evaporate to dryness, as directed on page 20, heating until fumes of sulphuric acid are given off in order to destroy all the carbonaceous matter. Or dissolve in nitric acid as above, evaporate to dryness, and heat on the tripod until the carbonaceous matter is destroyed; dissolve in 15 c.c. hydrochloric acid, add 12 c.c. dilute sulphuric acid as above, and evaporate until fumes of sulphuric acid are given off.

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[*] Liebig's Annalen, cxcviii. 318; Chem. News, xl. 207.

[†] Chem. News, xxxviii. 297.

Allow the dish to cool, add 100 c.c. water, and heat until the ferric sulphate is dissolved. Wash into a carefully graduated 300 c.c. flask, so that with the washings the solution may not exceed 200 c.c. in volume, and add a solution of sodium carbonate until the precipitate which is first formed dissolves only with difficulty. Then add slowly zinc oxide* suspended in water, shaking well after each addition until the iron is precipitated, which will be shown by the sudden coagulation of the solution. The precipitate will then settle, leaving a slightly milky supernatant liquid. Fill the flask exactly to the mark on the neck (300 c.c.), and mix thoroughly by pouring the entire contents of the flask into a large, clean, dry beaker, and back again into the flask, repeating this several times. Allow the precipitate to settle for a few minutes, and pour the solution through a large, *dry* filter. Fill a 200 c.c. pipette with this filtrate, which will, of course, represent exactly 1 gramme of the sample, run it into a flask of about 500 c.c. capacity, heat to boiling, and add from 2 to 5 drops of nitric acid (sp. gr. 1.2). Now add permanganate solution slowly from a burette, shaking after each addition to mix the solution and facilitate the collection of the precipitated hydrated manganese dioxide. When the reaction is nearly finished, the solution will be slightly colored by the permanganate, but the color disappears after shaking the flask and allowing it to stand for a moment. Finally, however, a drop or two will give the solution a permanent pink color, which will not disappear for several minutes. The number of c.c. of the permanganate solution used multiplied by the factor found (the iron factor of the permanganate multiplied by 0.2946) is the amount of manganese in the sample. If, during the addition of the permanganate, the solution should become cool and the precipitate fail to collect and settle quickly, heat the solution, but not quite to the boiling-point. This method is applicable for all samples except those containing very minute amounts of manganese. In working on spiegel, take .75 gramme, then, using two-thirds of the filtrate, the amount will be calculated on .5 gramme.

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* See page 58.

Williams's Method.

This method, which consists in precipitating the manganese dioxide by Ford's method, filtering, washing, dissolving in sulphuric acid with a measured volume of some reducing agent, such as oxalic acid or ferrous sulphate, and titrating the excess by permanganate, was first used by Williams.* Regarding the precipitate by potassium chlorate in a nitric acid solution as manganese dioxide, the reaction in dissolving it might be expressed thus: $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$, or $MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$. Therefore 1 molecule of manganese dioxide oxidizes 2 molecules of ferrous sulphate or 1 molecule of oxalic acid, and, the excess of oxalic acid or ferrous sulphate unoxidized having been determined by a solution of permanganate, the difference between this excess and the amount originally added is the amount oxidized by the manganese dioxide.

We therefore require two standard solutions, one of permanganate and one of ferrous sulphate, ammonium-ferrous sulphate, or oxalic acid. The permanganate solution used for iron determinations answers perfectly. A solution of ferrous sulphate is perhaps the most satisfactory, and is prepared by dissolving 10 grammes of the crystallized salt, $FeSO_4,7H_2O$,† in 900 c.c. water and 100 c.c. strong sulphuric acid. It will keep perfectly in a glass-stoppered bottle in the dark for a long time. One c.c. of this solution will be equal to about .002 gramme iron, or nearly .001 gramme manganese, and if the permanganate is of the usual strength, say 1 c.c. = .007 gramme iron, 1 c.c. of the permanganate will equal about 3.5 c.c. of the ferrous sulphate. The permanganate solution having been carefully standardized, transfer 50 c.c. of the ferrous sulphate solution by means of a pipette to a dish, dilute to about 1 litre, and run in permanganate solution from a burette, stirring constantly until the first permanent pink tint appears. The reading of the burette will give the value of 50 c.c. ferrous sulphate in permanganate, and consequently by a simple calculation its value in iron and manganese. Suppose, for instance, 1 c.c. permanganate solution =.0068 gramme iron, or (according to the proportion given above, 112 : 55 : : iron : manganese) =.00334 gramme manganese. Then if 14.1 c.c. permanganate = 50 c.c. ferrous sulphate, 100 c.c. ferrous sulphate will be equivalent to 28.2 c.c. permanganate. In using oxalic acid, dissolve 2.25 grammes of the crystallized acid, $H_2C_2O_4,2H_2O$, in 1 litre of water, and determine its strength by pouring 50 c.c. into the dish, diluting with *hot* water, adding 5 c.c. sulphuric acid, and titrating with permanganate.

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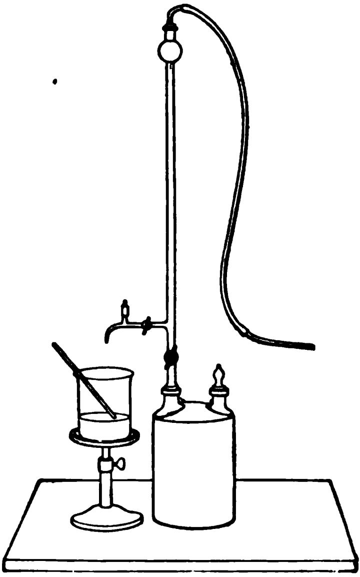
* Trans. Inst. Min. Engineers, x. 100.

† See page 56.

The details of the method are as follows. Weigh out 5 grammes of the sample of puddled iron, pig-iron, or steel, and proceed as directed on page 113 *et seq.;* but after filtering and washing the precipitated manganese dioxide with strong nitric acid, suck the precipitate as dry as possible, and then wash out the beaker in which the precipitation was made with cold water. Pour this water on the precipitate, and repeat the operation two or three times to get rid of all the nitric acid. Suck the precipitate as dry as possible, transfer it with the asbestos to the beaker in which the precipitation was made, measure into the beaker 100 c.c. of the standard ferrous sulphate solution (or 100 c.c. oxalic acid solution and 10 c.c. sulphuric acid), and stir until the manganese dioxide is all dissolved. When using oxalic acid it is necessary to heat gently to about 60° C. Wash the solution and abestos into the dish, dilute to about 1 litre (with oxalic acid use hot water), and titrate with permanganate. We will suppose, for example, that it requires 10.2 c.c. permanganate to give the permanent rose tint; then, as 100 c.c. ferrous sulphate = 28.2 c.c. permanganate, there would be the equivalent of 28.2 — 10.2 = 18 c.c. permanganate in ferrous sulphate oxidized by the manganese dioxide precipitate. One c.c. of permanganate being equivalent to .00334 gramme manganese, 18 c.c. = .06012 gramme manganese,

FIG. 54.



and, 5 grammes of the sample having been taken, .06012 ÷ 5 = 0.01202 × 100 = 1.202 per cent. manganese.

Fig. 54 shows a very convenient piece of apparatus designed by Mr. E. A. Uehling in 1884.*

It is especially useful when it is necessary to add rapidly a constant volume of a standard reagent; for instance, a measured excess of ferrous sulphate in volumetric determination of manganese after precipitation with potassium chlorate.

The burette-tube extends to the bottom of the Wolff bottle, which holds 2 litres. Enough air is supplied, without danger of dust or evaporation of solution, by means of a pin-hole drilled in the neck of the bottle and through the hollow glass stopper. The bottle may be blackened to preserve the solution from the action of light.

Spiegel and Ferro-manganese.

When working on spiegel or ferro-manganese, take .5 gramme of the sample and proceed in the same manner as directed for steel or iron; but it is better to use a standard solution of ferrous sulphate containing 30 grammes of $FeSO_4,7H_2O$ to the litre for very high ferro-manganese.

As there seems to be some uncertainty as to the exact composition of the manganese oxide,† the permanganate solution may be standardized as follows. Determine the absolute amount of manganese in a finely ground and well-mixed sample of spiegel or ferro-manganese by a gravimetric method, then treat .5 gramme of the same sample exactly as described above, and, having found the number of c.c. of permanganate that are equivalent to 100 c.c. of the ferrous sulphate solution, the amount of manganese in the sample divided by the number of c.c. of permanganate equivalent to the ferrous sulphate oxidized by the manganese oxide in the sample gives the value of the permanganate solution. Thus, if 100 c.c. ferrous sulphate solution require 28.2 c.c. permanganate to give the rose tint upon titration, the sample of spiegel contains 14.50 per cent. manganese, and the ferrous sulphate remaining after the solution of the manganese oxide in 100 c.c. requires 6.5 c.c. permanganate to give the rose tint upon titration (using .5 gramme of the sample, of which 1 gramme contains .1450 gramme manganese), the calculation would be as follows: 28.2 c.c. — 6.5 c.c. = 21.7 c.c. = .0725 gramme manganese, or 1 c.c. permanganate is equivalent to $\frac{.0725}{21.7}$ = .00334 gramme manganese.

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* Communicated to the author by Mr. A. L. Colby, of the Bethlehem Iron Company.

† Stone, Trans. Inst. Min. Engineers, xi. 323, xii. 295, 514; Mackintosh, Trans. Inst. Min. Engineers, xii. 79, xiii. 39.

Deshays's Method.[*]

This method is based on the fact that manganese nitrate, when boiled with excess of nitric acid and lead peroxide, is oxidized to permanganic acid, which is reduced again by a standard solution of sodium arsenite.

Dissolve .5 gramme of steel or pig-iron in a No. 0 Griffin's beaker, or in a test-tube, in 30 c.c. nitric acid (1.2 sp. gr.), and boil until solution is complete and the evolution of nitrous fumes ceases. Remove from the burner, add cautiously from 1 to 3 grammes of lead oxide, or red lead, free from manganese, and dilute with hot water to about 60 c.c. Heat the solution to boiling, and as soon as it commences to boil stand the beaker or test-tube aside and allow the lead salt to settle. When tolerably clear, decant the solution and boil the residue with 50 c.c. nitric acid and water (1 part acid to 3 parts water). Decant as before, and repeat the operation until the supernatant fluid is colorless. Filter the decantations through asbestos and titrate with a standard solution of sodium arsenite. The standard solution may be prepared of a convenient strength by dissolving 4.96 grammes of arsenious acid together with 25 grammes of sodium carbonate in water and diluting to from 2 to 2½ litres.

To standardize this solution, treat a steel containing a known amount of manganese, as described above, and calculate the value of each c.c. of the standard solution by dividing the per cent. of manganese in the steel by the number of c.c. required to destroy the color of the permanganic acid. Or take a measured quantity of a standardized solution of potassium permanganate and see how many c.c. of the sodium arsenite are equal to 1 c.c. of the permanganate solution. Then the value of th permanganate solution in iron, multiplied by $\frac{11}{56}$, is equal to its value i manganese, according to the equation,

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[*] Bull. Soc. Chim. de Paris, June 20, 1878.

$$10FeSo_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2C$$

or 10 atoms of iron correspond to 2 atoms of manganese, or 560 parts b weight of iron = 110 parts by weight of manganese. From this we g the weight of manganese to which 1 c.c. of the sodium arsenite is equi alent, from which the percentage of manganese in the steel is calculate

The details of this method have been very carefully worked out b Mr. H. C. Babbitt, of the Wellman Steel Company, who has used it f many years. He finds that ordinary red lead is quite as effective as th more expensive dioxide, and in an interesting series of experiments h shows that results obtained by filtering off a portion of the first solutio obtained by boiling with red lead and titrating are not accordant, and th the only method of getting thoroughly reliable results is by washing o all the permanganic acid and decanting as described above.

*Vanier's Modification.**

Dissolve .1 gramme of steel in a test-tube 10 inches (250 mm.) lon in 10 c.c. nitric acid (1.2 sp. gr.). Place the tube in a bath of calciu chloride which is kept at 140° C., and when the solution is complete an the nitrous fumes are expelled, add 10 c.c. of hot water and .5 gramme c lead dioxide and boil for four minutes. Arrange the bath so that the tes tube dips only about ½ inch (12 mm.) in the liquid, which will insu vigorous boiling from the bottom of the tube and prevent the lead dioxi from settling. Wash the contents of the tube into a wide-mouth two-oun (60 c.c.) bottle, so that the liquid shall be about 50 c.c. in volume. Pla the bottle in a centrifugal machine and rotate for two minutes. At t expiration of that time the liquid will be perfectly clear and the und composed lead dioxide compacted in the bottom of the bottle. Pour t clear solution into a small beaker and titrate with a standard solution of sodium arsenite until the pink color disappears.

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* Mr. George P. Vanier, of the Pennsylvania Steel Company, originated the use of a centri gal machine in this method which he has used since 1892. He finds it very satisfactory, and co stantly obtains in ten minutes results which are accurate within 0.02 per cent. Mr. Vanier h kindly furnished the details for this description.

The standard solution is prepared as follows:

Dissolve 20 grammes of pure arsenious acid and 60 grammes of sodium carbonate in 750 c.c. of hot distilled water, filter and dilute to 2 litres for a stock solution. Dilute 85.7 c.c. of this solution to 2500 c.c., and standardize with a steel in which the manganese has been carefully determined. This steel should contain approximately the same amount of manganese as the steels to be analyzed. In the event of being obliged to work on steels containing widely varying amounts of manganese it is best to use two standard steels, one containing about 0.4 per cent. and another 1 per cent. manganese, and to standardize the solution with both. In working on steels containing over 1.25 per cent. manganese .05 gramme of the sample should be taken for analysis. This method is particularly applicable to steels containing very small amounts of manganese.

Pattinson's Method (for Spiegel and Ferro-manganese).

This method is based on the precipitation of manganese as manganese dioxide, from a solution of manganous chloride, by calcium hypochlorite and calcium carbonate in the presence of ferric chloride (the presence of the latter salt or of zinc chloride being necessary to prevent the precipitation of any manganese in a lower state of oxidation than manganese dioxide).* Dissolve .5 gramme of spiegel or ferro-manganese in a No. 5 beaker in 15 c.c. nitric acid (1.2 sp. gr.), evaporate to dryness, and heat to destroy carbonaceous matter. Redissolve in hydrochloric acid, and boil down to remove nitric acid, but not to dryness, add a few drops of hydrochloric acid, and dilute with 10 c.c. water. Add calcium carbonate diffused in water until the solution becomes reddish by neutralization of the free acid, then add 5 or 6 drops hydrochloric acid and 100 c.c. of a solution of bleaching powder (calcium hypochlorite), made by treating 15 grammes of the powder with 1 litre of water and filtering. Now pour in about 300 c.c. of boiling water, which will raise the temperature of the solution to about 70° C., and add calcium carbonate, with constant stirring, until all the iron is precipitated.

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* Jour. Chem. Soc., xxxv. 365.

If the supernatant fluid has a pink color, due to the formation of a little permanganate, add a few drops of alcohol, which will reduce it. Filter on a large filter, wash until the filtrate is free from chlorides, place the filter and its contents in the beaker in which the precipitation was made, and add 100 c.c. of standard solution of ferrous sulphate, made as directed on page 118. When the precipitate is dissolved, transfer the solution to the dish, dilute to about 1 litre, titrate the excess of ferrous sulphate as directed on page 118, and calculate the percentage of manganese as there directed.

The Color Method (for Steel).

This method was first suggested by Pichard,* and was used essentially in its present form by Peters.† It requires one or more standard steels in which the manganese has been most carefully determined by a gravimetric method. When a number of samples are to be tested at the same time, as is usually the case, a bath like the one shown in Fig. 83 is necessary, but for the manganese color method it should contain a solution of calcium chloride, which boils at 115° C.‡ It is, of course, very necessary in a method of this kind that the operations should always be conducted as nearly as possible under the same conditions, and that the standard should always be dissolved at the same time as the samples to be tested. Weigh .2 gramme of each sample and of the standard, and place them in 8-inch test-tubes properly numbered. Pour into each test-tube 15 c.c. nitric acid (1.2 sp. gr.), cover each with a small glass bulb or very small funnel, and stand the test-tubes in the holes in the top of the bath, as shown in the sketch, Fig. 83. Heat in the bath at 100° C. until solution is complete. Pour the contents of a test-tube into a 100 c.c. tube, wash the test-tube out with cold water, adding it to the solution in the 100 c.c. tube, and finally dilute to the 100 c.c. mark. Mix thoroughly by placing the thumb over the top of the tube and turning it upside down several times. Draw out 10 c.c. of this solution with a pipette graduated to deliver 10 c.c., and let it run into the test-tube in which the solution was made. Treat each sample in this way, including the standard. The tube is merely washed out with water, but the pipette can best be cleaned by drawing it full from the 100 c.c. tube of the fresh sample, throwing the contents away, and filling it a second time to deliver into the test-tube. Stand the test-tubes in the rack again, add to each 3 c.c. nitric acid (1.2 sp. gr.), replace the bulbs or funnels, and stand the rack in the calcium chloride bath, the solution in which should now be boiling. When the *solutions in the test-tubes* begin to boil, add to each .5 gramme fine lead peroxide * and boil exactly five minutes. The lead peroxide can readily be measured by a small platinum spoon, made to hold about .5 gramme. It is necessary that the solutions in the test-tubes should boil, and it is easy to assure one's self of this fact by looking down into the test-tubes after the action caused by the addition of the lead peroxide has ceased. Remove the rack from the bath at the expiration of the five minutes, and stand it with the test-tubes in cold water, to cool the solutions and allow the insoluble lead salt to settle. The insoluble matter settles to the bottom of the tube in a heavy compact mass, leaving the supernatant fluid perfectly clean. When this occurs, which is usually within the space of half an hour, the solutions are ready to be decanted into the comparison-tubes.† In working on a number of steels we will suppose that we use two standards, one containing 1.2 per cent. of manganese, the other 0.6 per cent. As we weighed out .2 gramme, diluted the solution to 100 c.c., and took 10 c.c. in which to determine manganese, the amount taken corresponds to .02 gramme of the sample; and if we dilute the solutions of the standards after decanting into the comparison-tubes to 24 c.c., 1 c.c. will correspond to 0.05 per cent. in the high, and 0.025 per cent. in the low, standard. Decant each solution in turn into a comparison-tube, and dilute it until it has the exact tint and depth of color of the standard to which it most nearly approximates when first decanted. The percentage of manganese is found by multiplying the number of c.c. to which the sample has been diluted by 0.05 or 0.025, according to the standard with which it has been compared. If, however, the solution of a sample when first decanted and before dilution should be lighter in color than the lower standard, the latter may, after the other samples have all been finished, be diluted to 30 c.c., when each c.c. will correspond to 0.02 per cent. manganese, or, if this color is not sufficiently light, to 40 c.c., when each c.c. will correspond to 0.015 per cent. manganese. When even this color is not sufficiently light, a lower standard must be used for comparison, or a larger amount of the sample taken for solution. The comparison of the colors should be made in a camera or box, as shown in Fig. 86.

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* Comptes-Rendus Hebd. des Séances de l'Acad. des Sciences, December 30, 1872.

† Chem. News, xxxiii. 35.

‡ This latter modification is due to Mr. S. A. Ford.

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* See page 57.

† See Fig. 85.

The direct rays of the sun should not be allowed to shine on the solutions, and a northern light for the comparisons is preferable to any other.

DETERMINATION OF CARBON.

Carbon differs from all other elements in iron and steel in that it is supposed to exist in several conditions, and analytical chemistry supplies the means of distinguishing between at least two of these conditions. Until within a few years it was considered to exist in two forms, as graphite and as combined carbon. To Karsten is due the recognition of the fact that graphite is a form of pure carbon, and not a compound of carbon and hydrogen. It is always present as a mechanical mixture, and is thus distinguished from the other form, which was supposed to be combined chemically with the iron. Of late years the opinion has been growing that "combined carbon" exists in at least two conditions in steel, but as yet chemical methods for separating and distinguishing between these conditions have failed, so far as quantitative work is concerned. The analytical methods here given are:

The Determination of Total Carbon,
The Determination of Graphitic Carbon, and
The Determination of Combined Carbon.

DETERMINATION OF TOTAL CARBON.

We may divide the methods for the determination of total carbon in iron and steel into the following classes:

A. The direct treatment of the borings or drillings without previous separation of the iron, including:

1. Direct combustion in a current of oxygen (Berzelius).

2. Combustion with lead chromate and· potassium chlorate (Reg- lt).

3. Combustion with cupric oxide in a current of oxygen (Kuder- ich).

4. Combustion with potassium bisulphate (Bourgeois).

5. Solution and oxidation of the borings in sulphuric, chromic, and sphoric acids, the volume of the carbonic acid being measured borg, modified).

6. Solution and oxidation of the borings as in 5, the carbonic acid ıg weighed.

B. Removal of the iron by volatilization, and subsequent combustion he carbon, including:

1. Volatilization in a current of chlorine (Berzelius, Wöhler).

2. Volatilization in a current of hydrochloric acid gas (Deville).

C. Solution of the iron, and combustion or weighing of the residue, uding:

1. Solution in cupric-potassium chloride, filtration, and combustion of residue in oxygen (Richter).

2. Solution in cupric chloride, and combustion of the residue (Berze-).

3. Solution in iodine or bromine, and combustion with lead chromate, weighing, of the residue (Eggertz).

4. Solution by fused silver chloride, and combustion of the residue rzelius).

5. Solution of the iron in cupric sulphate, filtration, and combustion of residue in a boat in a current of oxygen (Langley).

6. Solution of the iron in cupric sulphate, and oxidation of the residue chromic and sulphuric acids (Ullgren).

7. Solution in dilute hydrochloric acid by the aid of an electric current, combustion of the residue (Binks, Weyl).

The most accurate method is undoubtedly the solution of the lings in the cupric-potassium chloride, and combustion of the due in oxygen gas.

A. 1. Direct Combustion in a Current of Oxygen.

This method requires the sample to be reduced to a very fine state of subdivision, otherwise some of the metal in the centre of the lumps becomes coated with oxide, and the carbon in it escapes combustion. Weigh from 1 to 3 grammes of the sample, and spread it as evenly as possible over the bottom of a platinum or porcelain boat, which should be at least 3 inches (75 mm.) long.* Place the boat in the porcelain tube B, Fig. 65, by means of the rod C, replace the stopper P, and turn on a current of oxygen from the cylinder O, the stopcock R being open and Q closed. The apparatus will now appear as in the cut. The description of the apparatus is given on page 142 *et seq.*, the only difference being that for this determination the U-tube H and roll of silver in the tube B are omitted. The precautions necessary in weighing the absorption apparatus, consisting of the bulb I and tube J, are also described fully on page 146. When the tube is full of oxygen, the absorption apparatus being weighed and attached, light the burners in the furnace, beginning at the forward end, and, when they are all lighted, maintain the temperature of the tube at a good red heat for forty-five minutes. Should the solution in the bulb I begin to recede, owing to the rapid absorption of oxygen by the metal in the boat, increase the flow of oxygen, and regulate it so that the gas may never pass through the bulb I more rapidly than three or four bubbles in a second. At the expiration of the forty-five minutes, shut off the current of oxygen at O, close the stopcock R, open Q, and start the current of air by opening T gradually, so that the water may flow into the lower bottle F. Turn down the lights in the furnace slowly, to avoid cracking the be, finally turn them out, and allow the current of air to run through he apparatus until the oxygen is expelled. This will usually be accomlished by running out half the water in the bottle F. Close the stopcock , remove the absorption apparatus, and weigh it. The increase of weight vill be carbonic acid, due to the carbon in the sample, and it contains 7.27 per cent. carbon.

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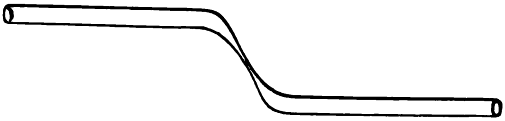
* I obtained better results by using a platinum boat about 6 inches (150 mm.) long provided with a cover of platinum-foil, through which a semicircular cut was made about every ½ inch (12 mm.). On raising these pieces to an angle of 45° they formed a series of little wings, which directed the current of gas flowing along the upper part of the tube down into the boat. It is difficult to get a sufficiently high temperature in a porcelain tube, but the results obtained in a platinum tube were very satisfactory. (See Jour. of Anal. and App. Chem., 1891, p. 125.)

2. Combustion with Lead Chromate and Potassium Chlorate.

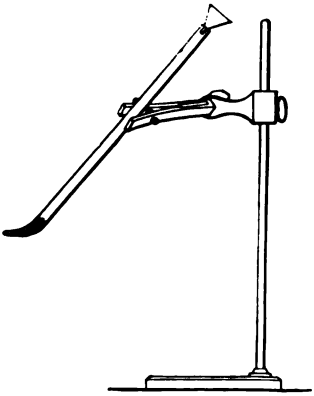
This method, like the preceding one, requires the sample to be ery finely powdered. Take a piece of combustion-tubing about 32 nches (800 mm.) long, ½ inch (12 mm.) internal diameter, and $\frac{1}{16}$ nch (1.5 mm.) thick in the walls; heat it in the middle by means f a blast-lamp until it softens, draw the ends apart slightly, and hen, keeping the ends parallel, draw it out, as shown in Fig. 55. Allow it to cool, scratch it n the middle with a file, nd break it. This gives wo tubes, each about 16 nches (400 mm.) long. Fuse he large ends slightly so as to round the sharp edges, but avoid ontracting the tube. Wash the tubes thoroughly, using a rod with piece of dark-colored silk or linen on the end; then if any lint emains on the inside of the tube it can easily be seen. Dry the ubes by heating them carefully and drawing air through them, then use the small ends and cork the large ends to keep out the dust. Veigh carefully from 1 to 3 grammes (1 gramme of pig-iron, spiegel, r ferro-manganese, 3 grammes of steel) of the sample, and grind it horoughly in a small mortar with 15 times its weight of fused and owdered lead chromate and 1½ times its weight of fused and owdered potassium chlorate or potassium bichromate. Potassium ichromate is to be preferred, as a little chlorine is sometimes given ff by potassium chlorate when used in this manner. Place the ombustion-tube in a stand, as shown in Fig. 56, and push down into the end, with a clean glass rod, a little ignited asbestos. The asbestos

FIG. 55.



should not be tightly packed, as it will prevent the air from passing in freely at the end of the operation. Place a small, dry, perfectly clean funnel in the end of the tube, and pour through it enough of the pure powdered lead chromate to fill the tube for about one inch of its length. Hold the mortar under the funnel so that anything that falls from it may go into the mortar, and charge the mixture into the tube by means of a small platinum spatula. Clean out the mortar by grinding in it two or three successive small portions of lead chromate, charging each into the tube through the funnel. Remove the funnel, cork the tube, and, holding it in a horizontal position with the tail up, tap it gently to get a clear space for the passage of the gas from one end of the tube to the other. Place the tube in the combustion-furnace, remove the cork, and insert in its place a smooth velvet cork, through the centre of which passes one end of a Marchand U-tube. The half of this tube nearest the combustion-tube contains anhydrous cupric sulphate,* and the other half granulated dried calcium chloride, the two reagents being separated by a small plug of fibrous asbestos loosely packed. Weigh, and attach the absorption apparatus and safety-tube. Apply suction at the end of the rubber tube on the forward end of the safety-tube, and draw a few bubbles of air through the potash-bulb. Allow the liquid to recede gradually; if it maintains its level in the bulb for a few minutes, the joints of the apparatus may be considered tight, but if it gradually falls, it is proof that there is a leak, and the joints must all be tightened. If, after pushing the cork as far as possible into the end of the combustion-tube and binding all the rubber connections, another trial still shows a leak, a fresh cork must be substituted. When the joints are all tight, light the burner at the

FIG. 56.



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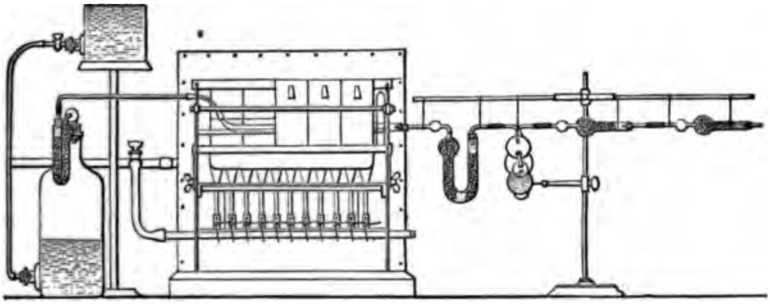
* See page 53.

forward end of the tube, and each burner successively as the flow of gas slackens, bringing the tube over each burner to a red heat before lighting the next one. Maintain the whole length of the tube up to the asbestos at a good red heat until the flow of gas entirely ceases. Then pass a piece of rubber tubing attached to a purifying apparatus well over the tail of the tube, which should be cool enough to be handled, break the point of the tail inside the tubing, lower the lights a little, and, by means of the aspirator-bottles, force about 1 litre of air through the apparatus. It will now appear as in Fig. 57. Turn out the lights, and detach and weigh the absorption apparatus, with the precautions mentioned on page 146. The increase of weight will be the carbonic acid due to the carbon in the sample. This contains 27.27 per cent. carbon.

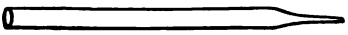
FIG. 57.



3. Combustion with Cupric Oxide in a Current of Oxygen.

Prepare the combustion-tube as directed in the last method, and pour on the asbestos in the end of the tube enough cupric oxide to fill the tube to the height of about an inch (25 mm.). Mix the weighed sample—from 1 to 3 grammes in a fine state of division—with at least twenty times its weight of finely powdered pure cupric oxide, charge it into the tube as directed on page 130, rinse out the mortar with a little more of the same material, and finally fill the tube to within an inch (25 mm.) of the end with granulated cupric oxide. Make the combustion exactly as directed in the last method (page 131). If the combustion is to be made in a current of oxygen, which is much the best plan, instead of drawing the combustion-tube out to a point and sealing it, it may be drawn out straight, as shown in Fig. 58. In this case, attach to the drawn-out end when the tube is in the furnace a purifying apparatus for oxygen and air, as shown in Fig. 65, and conduct the operation as directed on page 128.

FIG. 58.



4. Combustion with Potassium Bisulphate.

Certain classes of special material, such as ferro-chrome, cannot be decomposed by any solution, nor can the carbon be determined by direct combustion in oxygen.

The best-known method is by fusion with potassium bisulphate.

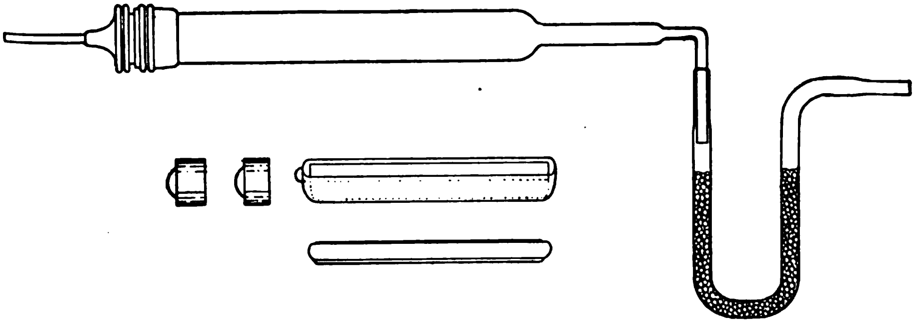
Place 1 gramme of the finely powdered sample in a porcelain boat about 150 mm. long and 30 mm. wide, and mix intimately with 30 or 40 grammes of fused powdered potassium bisulphate. Place the boat in a porcelain tube arranged as in Fig. 65. Connect the tube at the forward end with a flask containing a mixture of sulphuric and chromic acids, which can be heated. Connect with this a U-tube containing pumice saturated with chromic acid, then U-tubes, G and H, Fig. 65, filled as described on page 144. Attach the absorption apparatus and heat the forward end of the porcelain tube containing the sulphuric and chromic acids. Heat the tube where the boat rests very gently for two hours and gradually raise the heat to dull redness for half an hour, continuing the passage of the oxygen. Shut off the oxygen and pass the air for twenty minutes. Weigh the absorption apparatus in the usual way. The liberated sulphurous acid is oxidized by the cupric oxide or the chromic acid, and only the carbonic acid finds its way into the absorption apparatus.

In practice several difficulties arise that make the method unsatisfactory. The sulphuric acid, both that evolved from the potassium bisulphate as sulphuric acid by the cupric oxide and oxygen, acts on the rubber stoppers and sometimes carbonizes them sufficiently to give results several times greater than the actual carbon contents of the ferro-chrome. The spattering of the bisulphate, no matter how carefully the heat is applied, generally covers the inside of the tube around the boat and cements boat and tube together. The absorption of sulphuric acid by the cupric oxide causes the latter to swell, usually breaking the tube in the second, and sometimes while it is cooling in the first, determination.

To avoid these difficulties and sources of error I have devised the apparatus shown in the cuts.

Fig. 59 shows the platinum boats and cover. The smaller boat—150 mm. long and 25 mm. wide—fits inside the larger, and the cover is so arranged that any particles from the melting mass thrown on it run into the larger boat and thus keeps the tube itself perfectly clean.

FIG. 59.



The platinum tube shown in Fig. 59 is 400 mm. long and 30 mm. in diameter, and is closed with a ground joint at the rear. The forward end for a distance of 75 mm. is contracted to 12 mm. and filled with platinized asbestos. It is then further contracted to 6 mm. in diameter, and a piece of glass tubing filled with glass beads is fused to it after it is bent downward at an angle of 90°. The platinized asbestos facilitates the oxidation of the sulphurous acid evolved from the fused mass. The plugs are made of pumice wrapped with platinum-foil, and are pushed in after the boat. They serve to fill the back end of the tube and prevent the diffusion of the evolved gases and consequent condensation of sulphuric acid around the ground joint.

FIG. 60.

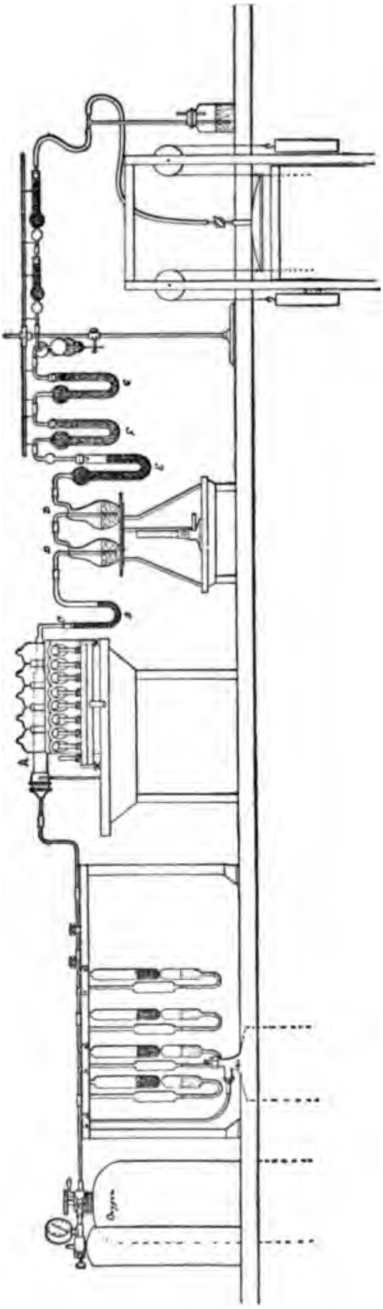
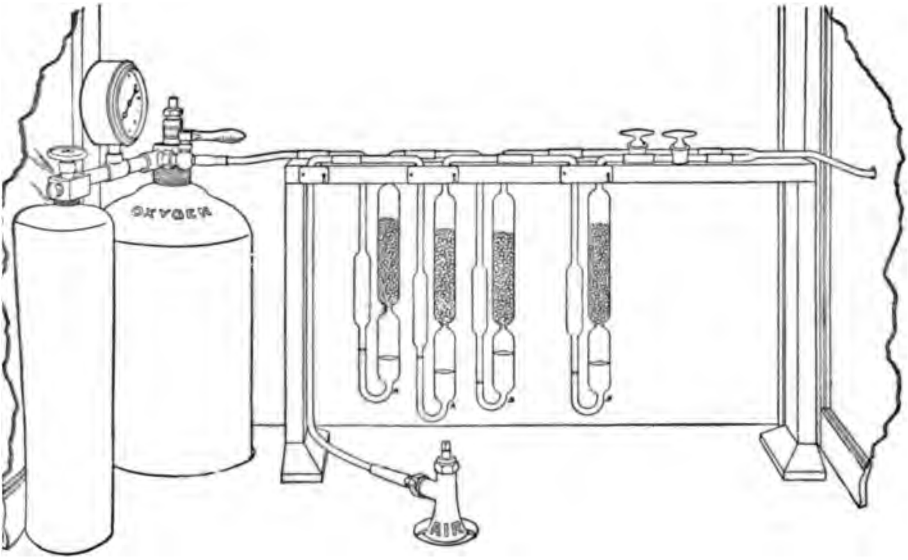


Fig. 60 shows the general arrangement of the apparatus. The purifyng apparatus for oxygen and air is shown in detail in Fig. 61. The tubes

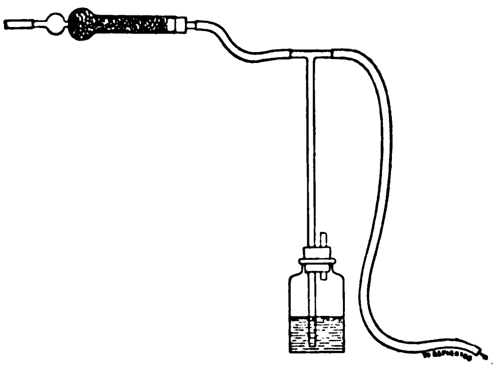
FIG. 61.



A and B contain respectively potassium hydrate and concentrated sulphuric acid. It is almost impossible with this form of tube to throw out the contained liquid either forward or backward. In Fig. 60, A is the platinum tube, B the glass tube containing beads fused to the contracted end of the platinum tube at C. D, D are glass flasks containing a solution of 150 grammes of chromic acid and 300 c.c. of strong sulphuric acid to the itre. These flasks stand on a copper plate and are heated by a Bunsen burner. The solution serves to oxidize any sulphurous acid that may have escaped oxidation in the contracted part of the platinum tube. E is a U-tube filled with glass beads, and acts as a condenser, F contains pumice saturated with chromic acid, and G contains dried calcium chloride. The absorption apparatus and guard tube follow. The latter is connected by a rubber tube with the gasometer, shown in the cut, which acts as an aspirator and serves to relieve the pressure in the apparatus, which, on account of the condensation of strong sulphuric acid in the tube B and the high specific gravity of the liquid in the flasks D, would otherwise be excessive. The details of this connection are shown in Fig. 62. The method is as follows:

Place 25 grammes of pure potassium bisulphate in the small boat (Fig. 59) and fuse it over a Bunsen burner or blast-lamp to destroy any carbonaceous matter, and allow it to cool. When cold spread 1 gramme of the finely ground sample evenly over the surface of the fused mass, place the boat inside the larger boat, arrange the cover, place the boats in the tube, insert the plugs, and close the tube with the ground joint. Connect the apparatus as shown in Fig. 60, and start a slow current of oxygen through the apparatus. Light the burners under the forward end of the tube which contains the platinized asbestos, and when this is red hot light the burner under the forward end of the boat and light the others successively until the tube is red hot for its entire length where the boat rests. Keep the tube hot for twenty minutes, replace the oxygen with air, turn out the lights, allow the air to run about thirty minutes, and detach and weigh the absorption apparatus with the usual precautions.

FIG. 62.



As a large amount of sulphurous acid is produced, it is necessary to heat the tube very gradually in order to keep an excess of oxygen in the tube to oxidize all the sulphurous acid. As the sulphuric anhydride does not condense readily, a slow current of gas is requisite, and a combustion requires about two hours and a half.

At the end of the operation the tube is opened and the plugs and boats removed. The fused mass is readily removed from the boats, which, with the cover, are washed and ignited ready for another combustion. About three determinations can be made in a day. Duplicate determinations agree within 0.01 per cent.

5. Solution and Oxidation of the Borings in Sulphuric, Chromic, and Phosphoric Acids, the Volume of the Carbonic Acid being measured.

The method given below for the determination of carbon in steel is generally used in the steel works laboratories in the eastern part of France, and I am indebted for the details to Monsieur H. A. Brustlein of Jacob Holtzer et Cie, of Unieux, at whose works and at those of the Aciéries de la Marine at Saint-Chamond the various improvements in the method have been worked out.

The method was first suggested by Wiborg,* but was very imperfect in its original form. The greatest improvement was suggested by Monsieur de Nolly, of the Laboratory of the Aciéries de la Marine at Saint-Chamond, and consists in the addition of phosphoric acid to the oxidizing mixture, by which the iron is much more rapidly dissolved and the use of a considerable amount of chromic acid is rendered possible without the evolution of a large volume of oxygen gas. M. Bénazet and M. Florence, of Unieux, substituted mercury for water in the original method.

The solutions employed are:

1. A saturated solution of chemically pure cupric sulphate.

2. An aqueous solution of chromic acid (1 gramme chromic acid to 1 c.c. water).

3. A mixture of sulphuric, phosphoric, and chromic acids made up as follows:

Solution of chromic acid (solution No. 2)	35 c.c.
Water	190 "
Concentrated sulphuric acid	750 "
Phosphoric acid (1.4 sp. gr.)	340 "

In preparing solution No. 2, add a few c.c. of sulphuric acid and heat to boiling to destroy any organic matter that may be present.

In preparing solution No. 3, heat it to boiling also for the same purpose.

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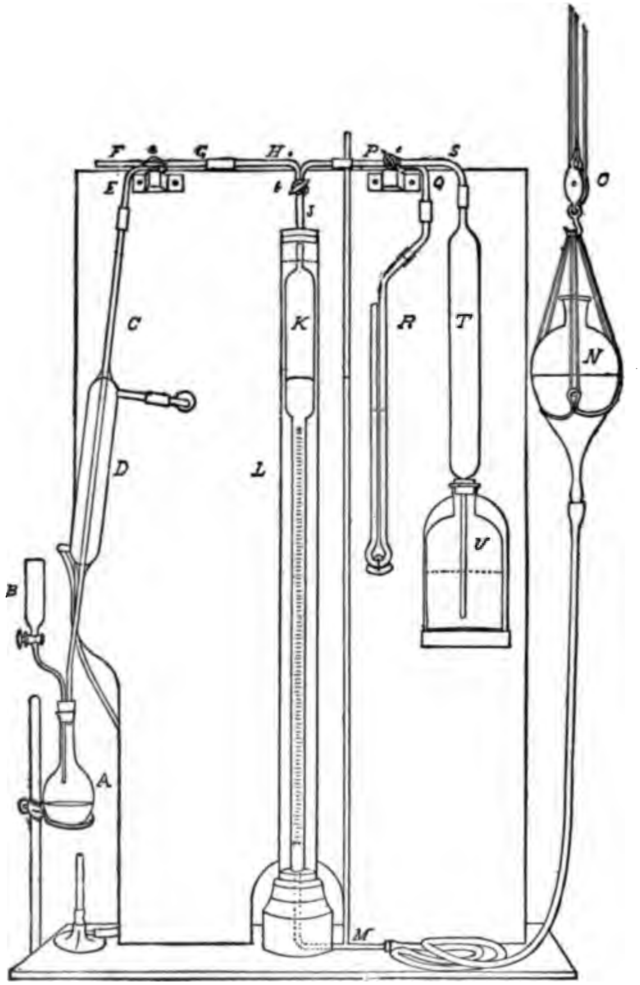
* Stahl und Eisen, 1887, p. 465.

The apparatus as shown in the sketch (Fig. 63) consists of a roun bottom flask, A, of 250 c.c. capacity, with a long neck. The flask is clos with a rubber stopper with two holes, in one of which is fitted the gla

FIG. 63.



stopper funnel B and in the other the tube C enclosed in the condenser through which a stream of water runs during the operation. The tub is connected with one tube, E, of a three-way stopcock, *a*, from which cond tube, F, opens into the air, and the third, G, connects with the tube of the three-way stopcock *b*. The second tube, J, from this stopcock is sed to the burette K, which is enclosed in the tube L containing water. he lower end of the burette connects with a tube, M, of small interior iameter, which serves as a level tube and is in the form of a T; it is conected with the mercury reservoir N, which is raised and lowered by the rrangement O. The third tube of the stopcock *b* connects with the tube of the stopcock *c*, the second tube, Q, of the stopcock *c* connects with e manometer R, and the third tube, S, with the pipette T, which runs to the bottle U. The tubes of the stopcocks *b* and *c*, the manometer be R, the level tube M, and the tubes of the pipette T are capillaries. he manometer tube R contains water, and serves to accurately adjust the vels when taking the reading of the burette K. When the manometer is hut off from the burette the approximate level is ascertained by means of e level tube M. The tube F of the stopcock *a* is used only in exceponal cases: first, when the evolution of gas is insufficient to carry the ercury far enough down the burette K, in which case air is drawn rough it into the burette; and secondly, when the evolution of gas is o great that it is necessary to make two absorptions in the pipette T, in hich case the residue from the first absorption is discharged through the be F. The pipette T, which is of about 400 c.c. capacity, contains a soluon of potassium hydroxide of 1.27 sp. gr. The bottle U is of about one tre capacity. The water in the containing tube L serves to keep the gas the burette at the ordinary temperature of the laboratory. It should be rotected from the heat of the burner and flask by a screen.

The operation is conducted as follows:

Connect the pipette T, by means of the stopcocks *b* and *c*, with the urette K, and, by lowering the mercury reservoir, fill the pipette with the otassium hydroxide solution, close the stopcock *c*, fill the burette K with ercury, and close the stopcock *b*. Weigh 1 gramme of drillings into the sk A, attach it to the apparatus, start the water through the condenser , and connect the flask with the burette K by means of the stopcock *a*. our 15 c.c. of the cupric sulphate solution No. 1 into the funnel tube B, d let it flow into the flask. Allow it to act long enough to form a superficial deposit of copper on the drillings (one or two minutes is sufficient), then add, through the funnel tube, 15 c.c. of solution No. 2 and 135 c.c. of solution No. 3. Heat the solution in the flask and raise it slowly to the boiling-point. By means of the reservoir, keep the mercury in the burette and in the tube M nearly level. The water condensed in the tube C drops back into the flask and keeps the liquid of the same density, while the properly cooled gases pass into the burette.

Allow the flask A to cool for about five minutes, and then run into it, through the funnel tube B, enough water to fill the flask and the tube to the stopcock *a*, thus forcing all the gas into the burette. Close the stopcock *a* and connect the burette, by means of the stopcocks *b* and *c*, with the manometer R, adjust the levels accurately, and take the reading of the burette. Then by means of the stopcock *c* connect the burette with the pipette T, and, by raising and lowering the reservoir N, pass the gas several times back and forth to cause the potassium hydroxide to absorb all the carbon dioxide. Finally connect the burette with the manometer tube R, adjust the levels, and take the reading of the burette.

The burette K should contain a few drops of water to insure the saturation of the gases with aqueous vapor. The difference between the two readings is the volume of the carbon dioxide. Observe the readings of the thermometer and barometer, and reduce the volume of the carbon dioxide to that which it would occupy in the dry state at 0° C. and 760 mm. pressure. (Table V.)

Multiply the volume of the gas so obtained by 0.0019663, and the result is the weight of the carbon dioxide in grammes.

6. Solution and Oxidation of the Borings as in 5, the Carbonic Acid being weighed.

Fig. 64 shows the details of the apparatus for carrying out this method. M is the U-tube for purifying the air. It contains fused caustic potash. A is the flask for oxidizing and dissolving the sample. The piece of glass tubing N bent at a right angle is drawn out slightly at the lower end, over which a piece of soft gum tubing is fitted, forming a stopper, which fits tightly in the top of the bulb-tube when air is forced through the

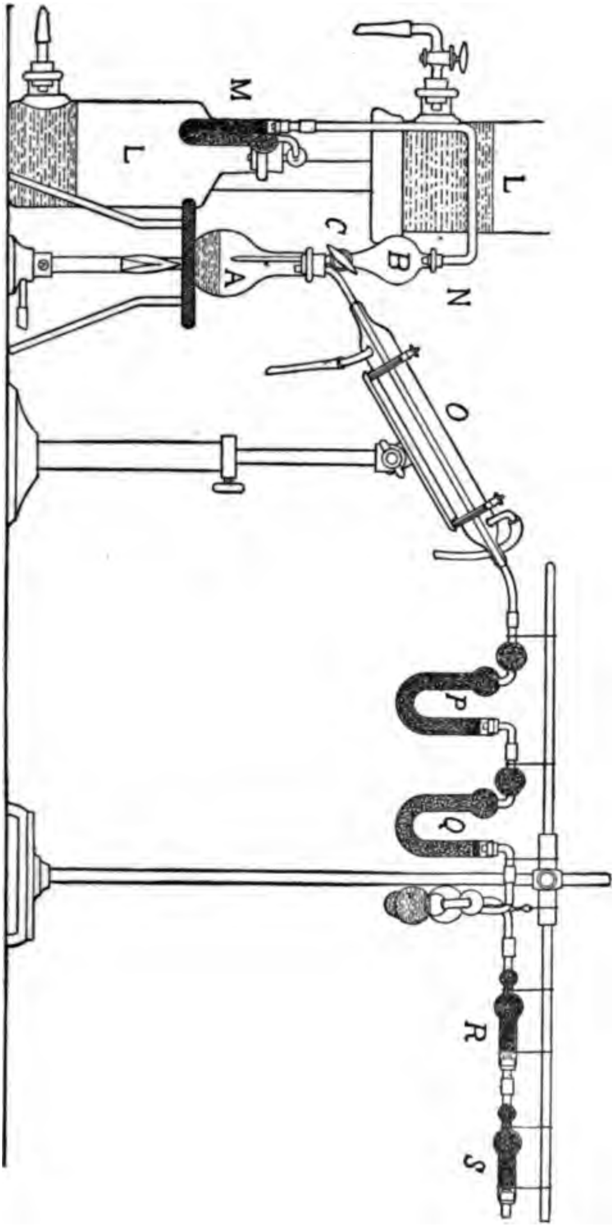


FIG. 64.

apparatus. B is a bulb-tube for introducing the reagents. The lower end is drawn out so that the orifice is quite small. O is a condenser, P contains anhydrous cupric sulphate, Q granular calcium chloride, and the small bulb of P and Q contains cotton-wool. The Liebig bulb and the tube R form the absorption apparatus, and S the safety-tube. Conduct the operation as described on page 139, pass two litres of air through and weigh the absorption apparatus as described on page 146.

B. 1. Volatilization of the Iron in a Current of Chlorine, and Subsequent Combustion of the Carbon.

Spread out evenly 1 gramme of pig-iron or 3 grammes of steel on the bottom of a porcelain boat about 3 inches (75 mm.) long, and treat it exactly as described on page 73 *et seq.* The boat when withdrawn from the tube contains the carbon, slag, and oxides, and nearly all of the non-volatile chlorides, such as manganous chloride. When the sample contains much manganese, it is necessary to treat the residue in the boat with cold water, filter it on a small plug of ignited asbestos, return it to the boat, and dry it before burning it off. As this adds very considerably to the time required for the determination, it is best to adopt some other method for the determination of carbon in such materials as spiegel and ferro-manganese. Introduce the boat into the tube B of the apparatus Fig. 65. This apparatus consists of a ten-burner combustion-furnace A, through which runs the porcelain tube B. This tube is about 25 inches (625 mm.) long and ¾ inch (18 mm.) internal diameter. It projects 6 inches (150 mm.) outside the furnace at each end, and the sheet-iron screens L prevent the heat from reaching the stoppers P and S. The tube is filled for a length of 6 inches (150 mm.), or from about the middle of the tube to the forward end of the furnace, with copper dioxide, which is best made by rolling up tightly a piece of coarse copper gauze 6 inches (150 mm.) long until it makes a roll *nearly* filling the bore of the tube, and heating it for an hour in a current of oxygen. A piece of thin sheet-silver 4 inches long, and forming a roll completely filling the bore of the tube, is placed just in front of the copper dioxide: it serves to absorb any chlorine given off during

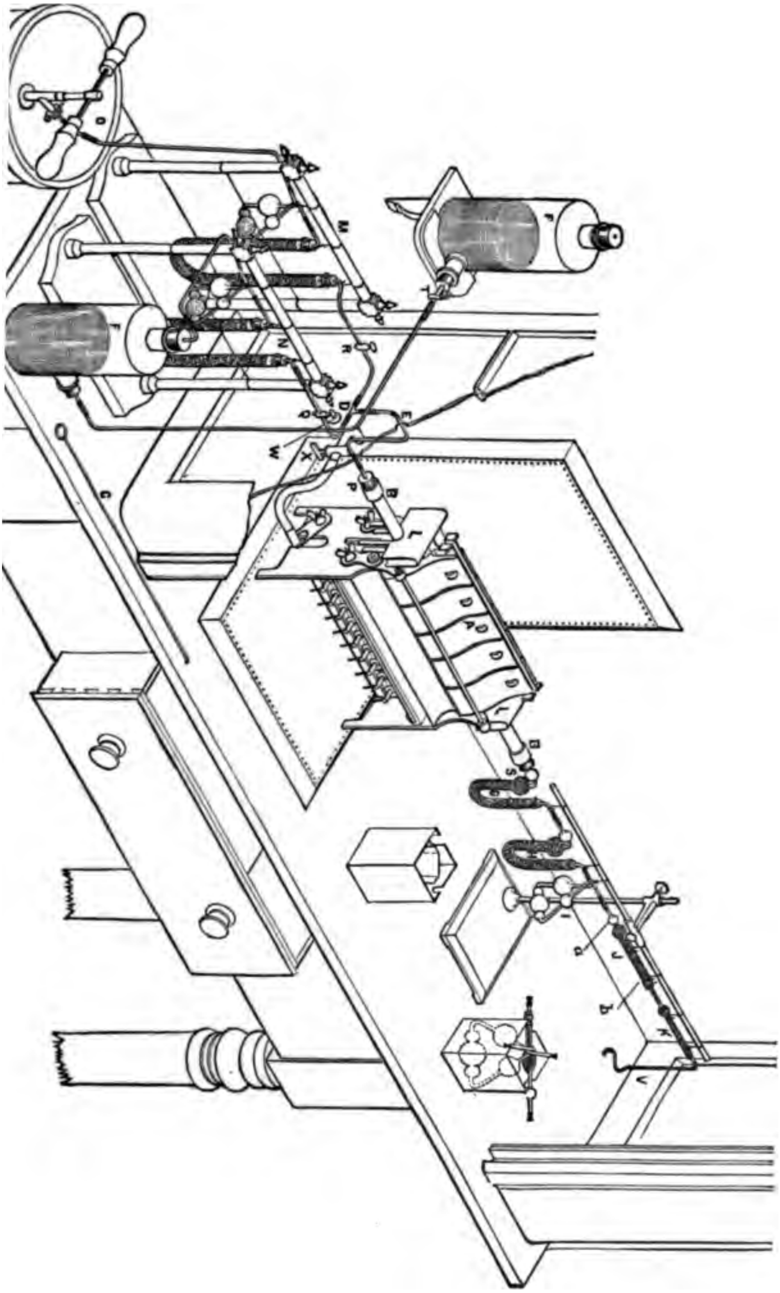


FIG. 65.

the combustion.* A roll of copper gauze two inches long, with a loop in one end, thoroughly oxidized, is pushed in after the boat containing the carbon. The cylinder O contains oxygen under pressure. The bottles F, F serve to force air through the apparatus to replace the oxygen at the end of the operation. The stopcock T serves to regulate the flow of water, and consequently of air. When all the water has run from the upper into the lower bottle, it is siphoned out of the latter and returned to the former.

The purifying apparatus M and N, for oxygen and air respectively, consist of Liebig potash-bulbs filled with solution of potassium hydrate (1.27 sp. gr.), and U-tubes, the sides next the potash-bulbs filled with dry pumice and the other sides with calcium chloride. The glass stopcocks Q and R shut off the purifying apparatus on their respective sides when the oxygen or air is passing through the other set. The T-tube D connects the two sets of apparatus, the third limb passing through the glass in the side of the hood, and connecting by means of the bent glass tubes with the rubber stopper P, which fits in the porcelain tube B. All the connections are made with glass tubes joined together by rubber tubing, the ends of the glass tubing being brought close together inside the rubber. This is to avoid carrying the oxygen or air through rubber tubing, which gives off volatile hydrocarbons. The Marchand U-tube G contains anhydrous cupric sulphate to absorb any hydrochloric acid which may be evolved during the combustion. It is joined to the tube B by a rubber stopper or by an abestos stopper,† made by pressing wet fibrous asbestos into a mould of the proper shape. When sufficient pressure is applied in making the stopper it becomes very hard. When dry it can be bored easily, and makes an excellent stopper for this purpose. The U-tube H contains granulated dried calcium chloride.‡ The absorption apparatus consists of the Liebig bulb I and the drying-tube J. I contains caustic potash (1.27 sp. gr.). It is filled by attaching a short piece of rubber tubing to one end and applying suction to it, the other end being immersed in the potash solution, which has been poured into a capsule. The end must be wiped dry with a little paper, and the inside of the tube dried in the same way. When filled, ulb should contain the solution as shown in Fig. 66. When attached : apparatus, the gas passes first into the large and, the bulbs being inclined, the gas bub- through the solution in the three bottom . It is fitted with a loop of platinum wire, own in Fig. 66. The drying-tube J contains calcium chloride. The small bulb *a*, Fig. ontains a plug of cotton-wool, and another of the same material is inserted after the ım chloride at *b*. K is a safety-guard tube, event moisture from getting into the tube J g the combustion. The short rubber tube used to draw a little air through to test the ıess of the joints. All the stoppers in the various U-tubes and drying-tubes are of rubber. The copper rod C is used to introduce the boats, etc., into the tube B, running the crooked end through the hole W in the glass side of the hood. When not attached to the apparatus, the ends of the potash-bulb I and drying-tube J are closed by little caps of rubber tubing * (Fig. 66) made like the tips for "policemen." When on the balance, however, they should be closed with short pieces of rubber tubing containing bits of capillary glass tubing, as shown in Fig. 67. The forward end of the dry- ıbe is closed in the same way. These openings are too small to the condition of the atmosphere to affect the weight of the bulbs

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* This roll of silver must occasionally be removed and ignited in a current of hydrogen to remove the chlorine.

† J. F. White, Amer. Chem. Jour., iii. 151.

‡ See page 52.

FIG. 66.

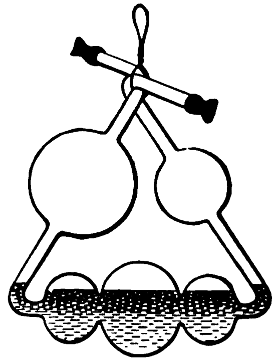
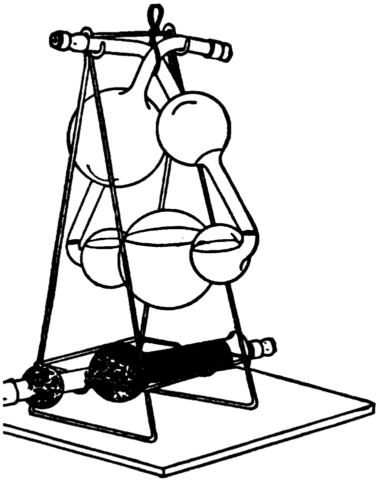


FIG. 67.



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* See page 31.

by loss or gain of moisture, but they serve to equalize the pressure and make it unnecessary to reopen the balance-case until the bulbs are weighed.

It is very necessary in filling the potash-bulb to avoid getting any of the solution on the outside of the bulb, and it is well to see that both the bulb-tube and the drying-tube are perfectly clean. Wipe the potash-bulb and drying-tube with a piece of linen, not silk (a clean linen handkerchief that does not leave lint on the glass is very good for this purpose), and place them on the balance.

The little wire stand shown in Fig. 67 is very convenient for holding the absorption apparatus in the balance, as it brings all the weight on the pan instead of putting the greater part on the beam alone, as is the case when the potash-bulbs are suspended from the hook on the end of the beam. Allow them to remain about thirty minutes to get the exact temperature of the balance, and weigh. Attach the absorption apparatus as shown in the sketch, Fig. 65, insert the boat in the tube by means of the rod C, pushing it up against the cupric oxide, insert the short roll of oxidized gauze as far as the inside of the screen L, and close the tube with the stopper P. Shut the stopcocks R and Q, and, by applying suction at V, draw a few bubbles through the potash-bulb I. When the liquid recedes in the potash-bulb, it should keep its level for a few minutes; if it does not, there is a leak in some of the connections, which must be discovered and stopped before proceeding with the combustion. When everything is tight, open R and start a slow current of oxygen through the apparatus. Light the two forward burners of the furnace, turning them low to heat the oxidized copper gauze, raise the heat gradually until the tube appears red, and then light the last burner to heat the short roll of oxidized copper gauze. As soon as this end of the tube is hot, light the third burner from the forward end, and a few minutes afterwards the fourth burner, which is directly under the forward end of the boat. Light each burner in succession from this one until all are lighted and turned high enough to heat the tube red hot. Allow them to burn for fifteen minutes, then shut off the oxygen, close R, open Q, and by means of the stopcock T start a current of air through the apparatus. By means of the gas-cock X lower all the lights of the furnace together very slowly, to avoid cracking the tube, and finally turn them out. About 1 litre of air should run through at the rate of three bubbles a second; this will about half empty the upper bottle L. Close T and Q, detach the absorption apparatus, close the ends of I and J with the little rubber caps, and, after wiping the bulb and tube gently with the linen handkerchief to remove any moisture caused by the handling, place them on the balance. Weigh with the same precautions as before; the increase in weight is carbonic acid, which contains 27.27 per cent. carbon. When several combustions are to be made in succession, as soon as the absorption apparatus is detached as directed above, remove the boat from the tube, replace it with another containing a second sample, attach a second absorption apparatus which has just been weighed, and proceed with the combustion. While the second combustion is in progress, the first absorption apparatus may be weighed, and the weight then obtained can be used for the first weight of the absorption apparatus for a third combustion. Before the absorption apparatus shall have increased .5 gramme in weight from the original weighing, the potash-bulb must be emptied and refilled with a fresh solution. When the final combustion for the day is finished, place a piece of glass rod in the open end of the connection of H, remove the boat from the tube B, replace the short roll of oxidized copper gauze in the tube, insert the stopper P, but not tightly, open R and Q, and loosen the stopper in the bottle F. Place pieces of glass rod in the ends of the safety-tube K, to prevent access of moisture. Whenever the apparatus has been out of use for a day, before making a combustion or set of combustions remove the piece of glass rod from the forward end of the U-tube H, insert in its place a piece of glass tubing drawn out at the forward end to a small orifice, start a current of oxygen through the apparatus, light the burners in the furnace, raising the heat very gradually, keep the tube at a red heat fifteen minutes, turn off the oxygen, start the air, lower the burners gradually, and pass a litre of air through the apparatus. It will then be ready for the combustion. In very damp weather it is almost impossible to get good results, the condensation of moisture on the absorption apparatus rendering the weighing extremely difficult even when the utmost care is used.

This difficulty may be overcome almost entirely by using another absorption apparatus of similar form as a counterpoise. This counterpoise should be arranged to weigh 2 or 3 grammes less than the absorption apparatus. The superficial area of the two being practically equal, the condensation on the two surfaces is the same.

The calcium chloride in the drying-tube of the absorption apparatus must frequently be renewed, as it absorbs the moisture carried over from the caustic potash, and the success of the operation depends upon the *oxygen and air leaving the absorption apparatus in the same hygroscopic condition as when they enter it.*

2. Volatilization of the Iron in a Current of Hydrochloric Acid Gas, and Subsequent Combustion of the Carbon.

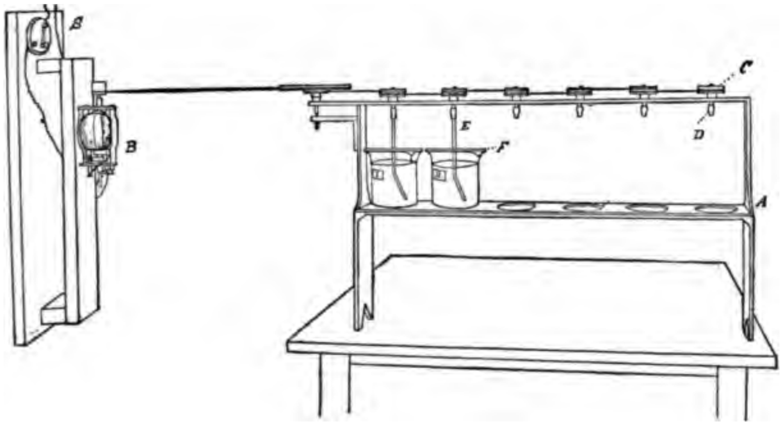
The process is exactly the same in this method as in that just described, a current of hydrochloric acid gas being substituted for one of chlorine. The apparatus for generating this gas is the same as the one used for chlorine, common rock-salt in pieces about as large as a filbert being substituted for manganese dioxide, and sulphuric acid, diluted with two-thirds its bulk of water, for hydrochloric acid.

C. 1. Solution in Potassium-Cupric Chloride, Filtration, and Weighing or Combustion of the Residue.

Place 1 gramme of pig-iron, spiegel, or ferro-manganese in a 400 c.c. Griffin's beaker, and add 100 c.c. of a saturated solution of potassium-cupric chloride and 7.5 c.c. hydrochloric acid. For steel or puddled iron, use 3 grammes and add 200 c.c. of potassium-cupric chloride solution and 15 c.c. strong hydrochloric acid. Stir the solution constantly with a glass rod for some minutes at the ordinary temperature. The more it is stirred the more rapid will be the solution of the iron and of the precipitated pper. The beaker, carefully covered, may now be placed on the top of air-bath or on a cool part of the sand-bath, but the solution should ver be heated hotter than 60° or 70° C., and it should be stirred as often practicable.

As the most tedious part of the determination of carbon in steel is quently that which has to do with the decomposition of the steel and e solution of the precipitated copper, particularly in the case of low els, the samples being nearly always in lumps, and it not being desirable separate these larger particles for fear that the fine stuff alone may not present a true average, the machine shown in Fig. 68 is very useful.

FIG. 68.

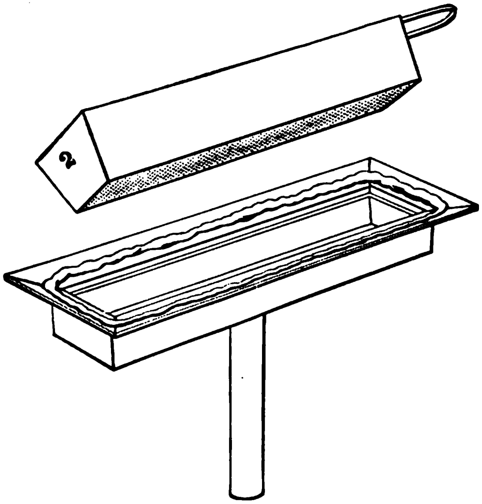


consists of a framework, A, of brass, cast in one piece for the sake of idity. It is fastened to the table by lugs and screws not shown in the t. The shelf on which the beakers stand has on it a piece of asbestos ard with holes to fit exactly the bottoms of the beakers to prevent them m moving. To further increase the stability of the beakers (which ould be of very heavy glass) their bottoms are ground on a glass plate th fine emery until they have a good bearing surface all around.

The tops, which are covered when on the machine with a plate of glass, ground on one side and perforated to allow the passage of the stirring-ds E, are likewise ground, so that when slightly moistened the ground glass prevents almost entirely all movement of the covers on the beakers when the machine is in motion. .

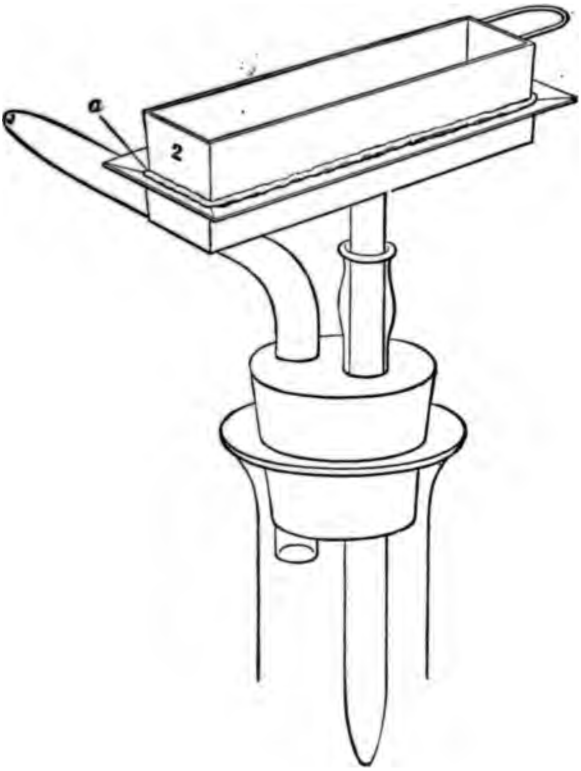
The small wooden pulleys C are fitted with brass spindles, which run through the upper cross-piece and have on their lower ends pieces of rubber tubing, which serve to hold the stirring-rods. The stirring-rods are bent as shown in the cut, to give the proper motion to the liquid. A small motor, B, adapted to the strength of the current, furnishes the requisite power. The motor, if properly wound, may be attached to an ordinary incandescent lighting current, but a sewing-machine motor run by a dipping battery of three bichromate cells is sufficient to give the necessary number of revolutions.

FIG. 69.



The fact that it is not only unnecessary to use a neutral solution, bu that the use of a neutral solution gives inaccurate results, seems now t be thoroughly established b the experiments of the Amer ican members of the Internation Steel Standards Committee. Th best practice is to add about 1 per cent. of hydrochloric aci to the solution of the potassium-cupric chloride. The reactions occurring may be considered as $Fe + CuCl_2 = FeCl_2 + Cu$ and $Cu + CuCl_2 = 2CuCl$. The part taken by the potassium chloride does not seem very clear, but the fact remains that the precipitated copper is much more soluble in the double salt than in any other menstruum. When the precipitated copper is all, or very nearly all, dissolved, which is usually the case in half an hour after the solution of potassium-cupric chloride is added to the drillings, run a little of the acidulated double chloride around the sides of the beaker by means of the rod, wash the rod over the beaker with a jet of water, and let the beaker stand for a few minutes to allow the carbonaceous matter to settle.[*] The best form of filtering-apparatus is shown in the annexed sketches. It consists of the perforated platinum boat (Fig. 69), which fits in the platinum holder. To prepare the boat for use, place it in the holder, as shown in Fig. 70, attach the pump, but do not start it. Fill the boat with prepared abestos[†] suspended in water, pour enough around the outside of the boat to fill the space *a*, Fig. 70, and start the filter-pump. Continue pouring the suspended abestos into the space *a*, Fig. 70, until enough

FIG. 70.



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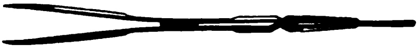
[*] Barba suggests adding to the solution ignited asbestos in water to make the carbonaceous matter settle and to prevent its clogging the filter. This is a most admirable suggestion and should be generally adopted.

[†] See page 27.

is drawn into the joint to make a good packing. By pressing it in all round with a spatula the joint may be made very tight. Pour enough of the suspended asbestos into the boat to make a good, thick felt, and press it down firmly all over the bottom of the boat with something like the square end of a lead-pencil, to make it compact. Detach the pump, remove the boat from the holder carefully so as to leave the packing on the sides of the holder, and move it up with the end of a spatula, so that it will remain as shown in Fig. 69. Place another boat in the holder, press the packing into the joint *a*, Fig. 70, with the end of a spatula, fill the boat with suspended asbestos, and start the pump. If necessary, pour a little of the finer suspended asbestos fibre into the joint to make it perfectly tight, and prepare the felt in the boat as before. Dry the boats, and ignite them in the combustion-tube, two at a time, in a current of oxygen. Fit one of these prepared boats in the holder, press the packing into the joint as before, first moistening it slightly if it has become dry, start the pump, and pour into the boat enough suspended asbestos, which has been ignited in oxygen, to form a thin film on the top of the felt. This film will hold the silica, ferric phosphate, etc., from the carbonaceous residue, and, after the combustion, will usually turn up at the edges, so that it can readily be detached from the main felt, leaving the boat ready for another filtration.

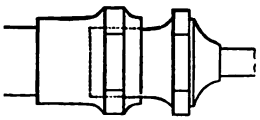
The boat being thus prepared, pour into it the solution of the iron or steel, guiding the stream by a small glass rod held against the tip of the beaker. The solution, if the joint *a*, Fig. 70, is tight, and the pump works well, will usually run through the felt as rapidly as it can be poured into the boat. When the supernatant fluid has all run through, transfer the carbonaceous matter to the boat by a fine stream of cold water from a washing-flask. Pour into the beaker about 10 c.c. of dilute hydrochloric acid, run it all around the inside of the beaker by means of the rod to dissolve any adhering salt, wash the glass rod and wash down the sides of the beaker with a jet of water, and decant the acid into the boat, filling it almost up to the edge. Wash the carbonaceous matter in the boat thoroughly with hot water by filling the boat from the beaker and allowing it to suck through dry, but do not attempt to throw a jet of water into e boat from the washing-flask, as it will be almost certain to throw some : the carbonaceous matter from the boat or cause it to crawl over the ide. In decanting the water from the beaker, the lip must not be allowed o touch the surface of the liquid in the boat, as a film of carbonaceous natter will run up the inside of the beaker. Pour a little dilute acid into he joint between the boat and holder, allow it to suck through the packng, and wash it several times with hot water. The carbonaceous matter om pig-iron, puddled iron, spiegel, ferro-manganese, and ingot steel sually washes like sand, but that from steel which has been hardened, mpered, hammered, or rolled is apt to be more or less gummy, stopping e filter and rendering the filtration and washing prolonged and tedious. : is also apt to adhere more or less to the sides of the beaker, and must e wiped off by a little wad of ignited fibrous asbestos, held in a pair of latinum-pointed forceps like those shown in Fig. 71.

FIG. 71.



This wad is then placed in the boat. When the carbonaceous matter ; thoroughly washed and sucked dry, detach the pump, remove the boat rom the holder, wipe the outside arefully with a piece of silk, place it ı a dish covered with a watch-glass, nd dry it in a water-bath or an air-ath at 100° C. When dry, insert the boat in the tube (Fig. 65), and burn ff the carbon as directed on page 146. Instead of the porcelain tube, a latinum tube of the dimensions shown in Fig. 73 may be used to very reat advantage. The rear end has a ground joint (Fig. 72), which may e made perfectly air-tight. The tube has a strengthening band of German silver at B, Fig. 73, and the part P, which is of phosphor-bronze, is ground in. To prevent the tube from sagging when it is hot, the rear end is supported at P, Fig. 73, by a wire from the top of the hood. A piece of platinum auze ½ inch long (12 mm.), rolled up rather loosely, fills the forward end f the tube, then the tube is filled for a distance of about 6 inches (150 m.) with granular copper dioxide, followed by another piece of platinum auze of the same size as the first, and a similar roll 2 inches long, with a

FIG. 72.



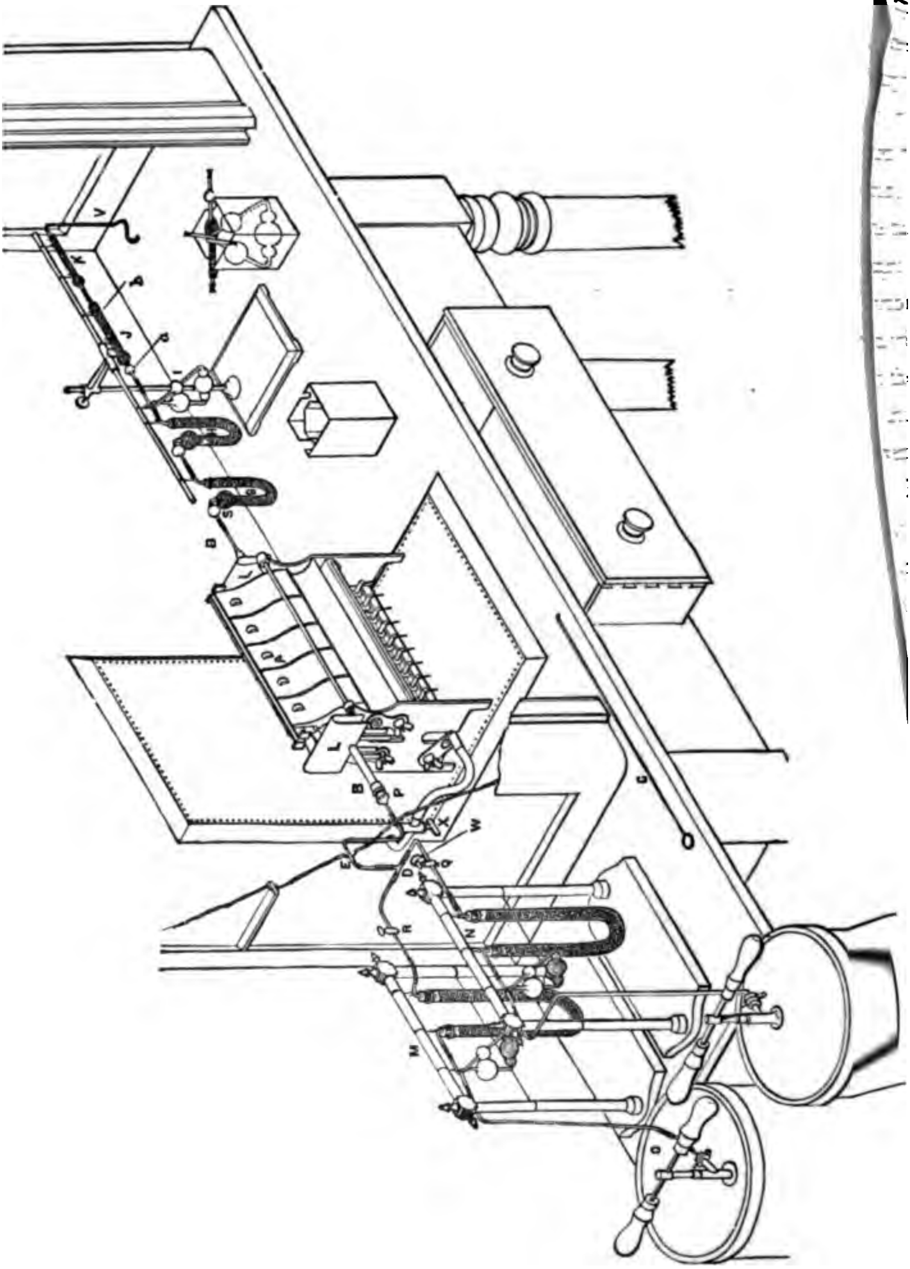


FIG. 73.

oop, is pushed in after the boat, the rear end coming just forward of the screen L. The limb of the U-tube G nearest the platinum tube contains anhydrous cupric sulphate * and the forward limb anhydrous cuprous chloride.† H contains dried, *not fused*, calcium chloride, and in the bulb next to G is a small wad of cotton-wool. G and H are called the purifying train, and when the apparatus is not in use they should be detached from he tube and the ends closed with pieces of glass rod. The object of the uprous chloride is to absorb any chlorine that may come over during the ombustion. If any should come over it would be mixed with hydro- hloric acid and moisture, and all then would be absorbed by the salts n the tube G. If the carbonaceous residue is properly washed it will be ound necessary to renew the salts in G only after it has been used for wenty-five or thirty combustions.‡

Before making a combustion, or series of combustions, the tube hould be well burned out by heating it to redness and passing a urrent of oxygen through the apparatus, heating the small tube S ed hot at the same time by means of a small blast-lamp or Bunsen urner. During this operation fumes of sulphuric acid issue from he end of S, and usually, when the flame of the lamp is carried ut to this point, it is colored green, showing that a small amount f copper salt is also volatilized. In making a combustion the plati- um should not be heated above a low red, as at a high temperature latinum becomes permeable by carbonic acid. The burners in the urnace should be lighted in the order directed on page 146, and, fter they are all lighted, ten minutes' time is ample to burn off the arbonaceous matter in the boat. From the time of putting in the oat, fifty minutes' time is ample for finishing the combustion, including he displacement of the oxygen by air.

Instead of the arrangement of bottles F, F for forcing air through he apparatus shown in Fig. 65, a second cylinder containing air under pressure, as shown in Fig. 73, is much more satisfactory, as the current can be controlled with perfect accuracy, the trouble of siphoning the water from the lower bottle is avoided, and there is no danger of passing gases or fumes from the laboratory into the apparatus.

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* See page 53.

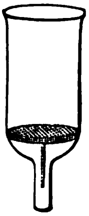
† See page 54.

‡ For a detailed account of the experiments on determination of carbon in steel, see Prof. angley's paper, Transactions of the Inst. of Mining Eng., Pittsburg International Meeting, ctober, 1890, and Jour. of Anal. and App. Chem., 1891, page 121.

The time required when using a porcelain tube is somewhat longer, owing to the danger incurred of cracking the tube if the heat is increased or diminished too rapidly. A platinum tube shorter than the one here figured is not to be recommended, as it cannot contain enough oxygen to burn the carbon to carbonic acid, and a consequent loss is often unavoidable. Duplicate results by this method should rarely vary more than .005 of a per cent. carbon. When using 3 grammes of the sample, the percentage of carbon is obtained by dividing the weight of carbonic acid by 11 and multiplying by 100.

Instead of the perforated boat and holder described above, the carbonaceous residue may be filtered in a small platinum tube fitting inside the combustion-tube. It is made as represented in Fig. 74. The small perforated disk of platinum rests on a seat in the tube as shown in the sketch. The felt in the disk is prepared in the same way as directed for the boat, and, after drying the carbonaceous residue, the disk is moved upward in the filtering-tube, to allow the gas to pass through the filtering-tube during the combustion. The boat has several advantages over the filtering-tube, the principal one being that the boat has a much larger filtering-surface, and, besides, there is no danger of the felt being disturbed during the filtering, while the disk in the tube may be loosened in its seat and allow some of the carbonaceous matter to pass around it. If the boats when not in use are kept carefully covered, the same felts may be used for a large number of filtrations; but occasionally they become clogged, and then it is better to renew them.

FIG. 74.



Instead of either of these forms of filtering-apparatus, a simple glass tube, as represented in Fig. 75, may be used. The closely coiled spiral of platinum wire fits in the tube as shown in the sketch. On this is placed a rather thick layer of ignited long-fibre asbestos ignited asbestos suspended in water is poured over it to make a felt. The tube may be used in a stand, as represented in Fig. 76,

Fig. 75.

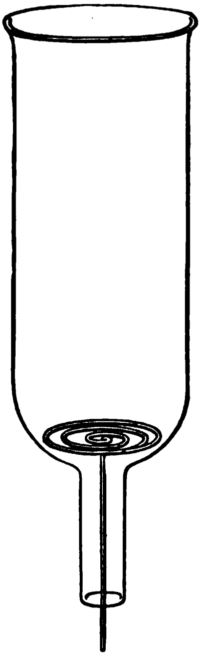
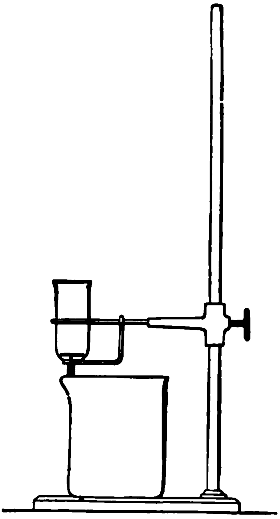
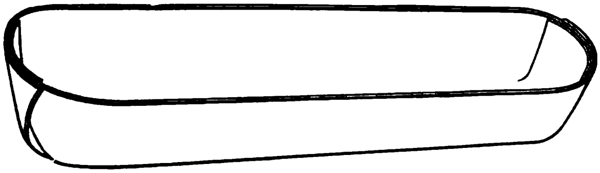


Fig. 76.



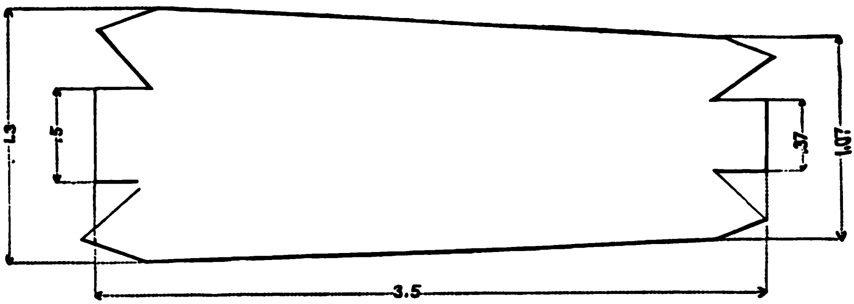
: may be used with the filter-pump under very gentle pressure. r and wash the carbonaceous matter, and while still moist transfer the boat (Fig. 77) by opening out the sides of the boat, inverting

Fig. 77.



ube over it, and allowing the felt and spiral to slide out of the Wipe off any carbonaceous matter that may remain on the of the tube, or that may have adhered to the spiral in removing it, with little wads of fibrous asbestos held in the forceps (Fig. *71*). Place these wads in the boat, bend the sides of the latter into their proper shape, dry the boat and contents at 100° C., insert the boat in the porcelain or platinum tube, and burn off the carbonaceous matter as before directed. This boat is made by cutting a piece of platinum-foil in the shape shown in Fig. 78, and bending it up over a brass former into the shape shown in Fig. 77.

FIG. 78.



Instead of burning the carbonaceous matter in a current of oxygen, it may be burned by sulphuric and chromic acids in the arrangement shown in Fig. 79. P′ is an empty U-tube, O is a tube containing silver sulphate dissolved in strong sulphuric acid, P contains anhydrous cupric sulphate, Q granular dried calcium chloride, a Liebig bulb and drying-tube R constitute the absorption apparatus, S is the safety-guard tube, and L, L constitute the arrangement for passing air through the apparatus. The air is freed from carbonic acid in passing through the U-tube M filled with lumps of fused potassium hydroxide. Transfer the carbonaceous matter and asbestos to the flask A, insert the stopper carrying the bulb-tube B, close the stopcock C, and connect the apparatus as shown in Fig. 79, including the weighed absorption apparatus. See that the joints are all tight, and then pour into B 10 c.c. of a saturated solution of chromic acid, admit it to the flask A by opening the stopcock C, and then pour into B 100 c.c. strong sulphuric acid which has been heated almost to boiling with a little chromic acid. Let this run into A slowly, connect the

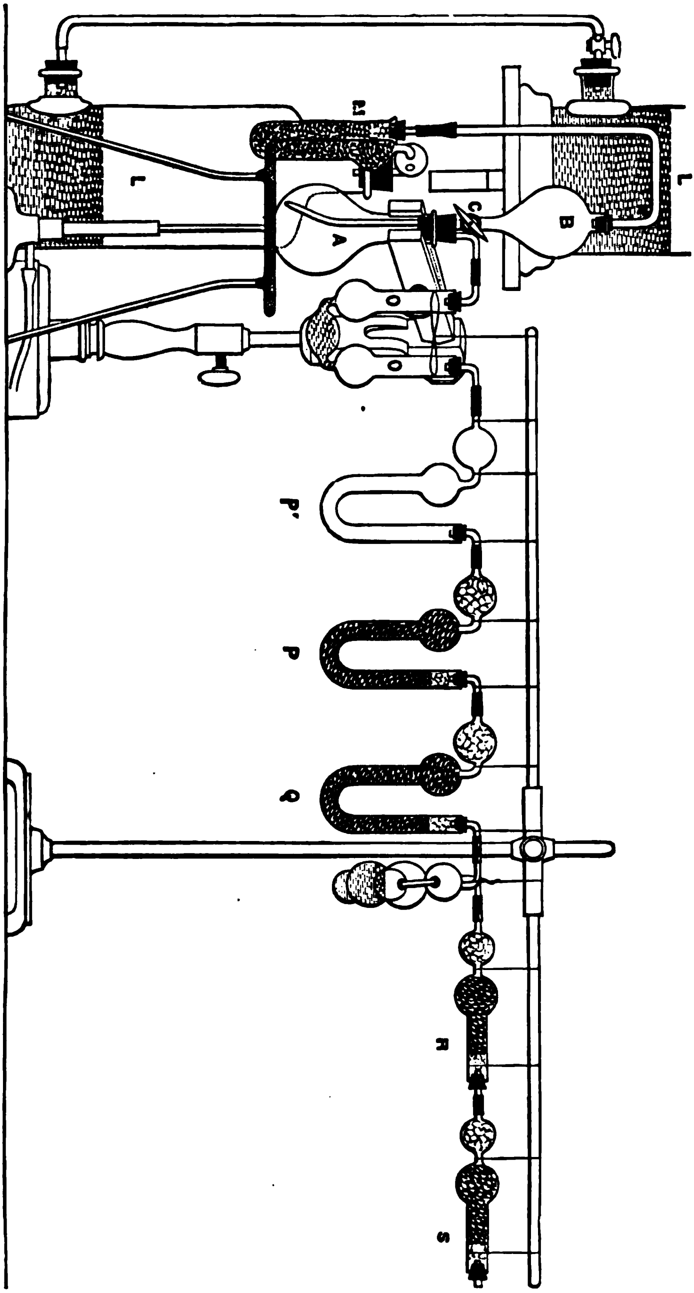


FIG. 79.

air apparatus by the tube N, and start a slow current of air through. Light a very low light under A, and increase it gradually until the liquid is heated to the boiling-point. Gradually lower the light while the current of air continues to pass, and when about 1 litre of air has passed through the apparatus after the light is extinguished, detach and weigh the absorption apparatus, with the precautions mentioned on page 146.

The carbonaceous residue may also be weighed directly instead of being burned off. In this method, filter on a Gooch crucible or on counterpoised filters,* dry at 100° C., and weigh. Burn off the carbonaceous matter and weigh the residue: the difference between the two weights is carbonaceous matter, which contains about 70 per cent. of carbon † in steel or iron free from graphite. Of course this method of direct weighing is applicable only to samples when all the carbon is in the so-called combined condition.

Modifications of Job and Davies. ‡

The following are the principal details of the apparatus (Fig. 80):

A combustion-furnace, K, nine inches in length, having three Bunsen burners with spreaders.

A Berlin porcelain combustion-tube, G, twenty inches in length and three-fourths inch inside diameter, containing about four inches in length of closely rolled copper gauze, I, fitting at first rather loosely in the tube, and thoroughly oxidized prior to use,—exactly as in the old method,—with pieces of clay pipe stem between the cupric oxide and the end of the tube to prevent the former from being forced out of place when the boat runs up against it in the determination. A piece of platinum-foil as long as the boat, rolled into tubular form, fitting closely in the combustion-tube and pushed into place next to the cupric oxide, with the edges somewhat bevelled so that the boat when quickly pushed in with the wire will run up smoothly upon the foil. This contrivance has been found to letely prevent cracking of the por- tube, even when a cold boat is t into the red-hot tube.

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* See page 29.

† American Chem. Jour., iii. 245.

‡ Prepared for this book by Messrs. Robert Job and Charles T. Davies from a paper read before the Philadelphia Section of the American Chem. Soc., September 13, 1900.

sbestos shields at H, H, through h the tube passes, prevent possible ng of the ends.

six-inch U-tube containing pieces of ughly dehydrated cupric sulphate t one-eighth inch in diameter in one F, and dehydrated cuprous chloride e same size in the other, E, with a piece of glass wool between them lso upon the tops, as recommended lair.

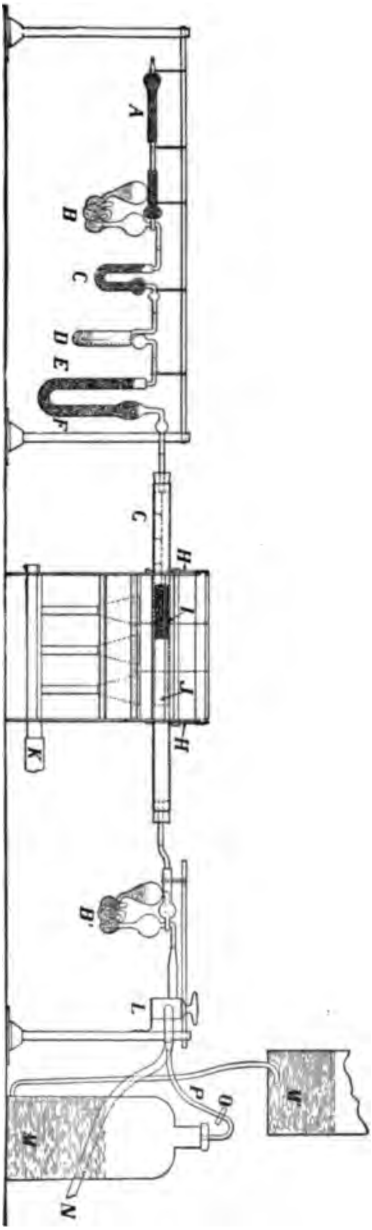
small bubble-tube, D, containing t 10 c.c. of a saturated solution of sulphate in sulphuric acid of 1.40 r.

four-inch U-tube, C, containing ughly dehydrated granular calcium ide in particles of about one-eighth in diameter, free from powder.

otash bulbs B, with calcium chloride attached, the bulbs being about one in diameter and one and a quarter s high; the cluster when filled ready se containing about 35 c.c. of potas- hydrate (1.27 sp. gr.), and weighing, ding the calcium chloride, about 80 mes; the calcium chloride tube is two and a quarter inches long and alf inch in diameter.

he potash bulbs B′ are exactly the as B, but the calcium chloride

FIG. 80.



tube remains empty and serves merely to prevent any possibility of spattering of potassium hydrate solution into the combustion-tube.

The three-way cock L leads to the oxygen tank N, containing oxygen free from hydrocarbons, and to the air-pressure P, the latter being produced by two two-litre bottles, M and M′, and the pressure regulated by a screw-clamp, O.

In the regular determinations 3 grammes of steel are dissolved in about 200 c.c. of double chloride of copper and potassium acidified with hydrochloric acid, and filtered upon a platinum boat, washed with dilute hydrochloric acid, then with water, and dried at not exceeding 110° C. after the usual manner.

In heating the furnace, the middle burner is lighted and turned up one-half for five minutes, then full; at the same time the two other burners are turned up one-half, and after five minutes given the full flame. The tube will be red hot in about fifteen minutes from the start, and is ready for the day's determinations without further attention.

The weighed potash bulbs B are then connected in place, the gum stopper next to B′ removed, and the boat in the combustion-tube, if present, quickly hooked out upon a porcelain tile with a copper wire. The oxygen is then started through the purifying potash bulbs B′ at the rate of about four bubbles per second, the dried boat for the determination removed from the oven, pushed quickly into its position, and the gum stopper inserted promptly. The current of oxygen is then let pass for seven minutes at the same rate of speed, though only about three minutes are actually required ordinarily for the combustion. The oxygen is then shut off, the three-way cock turned, and the air passed for twelve and a half minutes at the rate of six or seven bubbles per second, or as fast as the bubbles can pass and remain separate, about one litre of air being passed in this time.

The entire combustion is thus finished within twenty minutes, when the bulbs are removed and another set, previously weighed, are connected and the second combustion proceeded with.

The potash bulbs should be refilled after absorbing about 2.5 grammes of carbon dioxide, and the calcium chloride tube at the same time. Care ust be taken to have the calcium chloride thoroughly dehydrated, in ıall eight-inch granular form, without powder, and shaken down as com.ctly as possible by tapping lightly with the finger upon the tube and ling as needed until full. A very little cotton batting is placed at either d. The calcium chloride tube C immediately preceding the weighed tassium hydrate bulbs should be filled in the same manner, and should filled with freshly dehydrated calcium chloride after about fifty deterinations, or when the calcium chloride in the end nearest the silver lphate solution becomes slightly moist.

In practice the greater part of the calcium chloride may be used over d over again, dehydrating when removed by heating in an iron or porcein dish.

The copper salts in the U-tube should be thoroughly dehydrated by ating to a temperature of about 110° C. and aspirating slowly with air. is can be accomplished very easily by placing the U-tube flat upon the am table and attaching slow suction for about one hour. This should done as soon as the cupric sulphate tends to become blue or green upon e top of the arm F of the U-tube. When ready for use the cupric lphate should be very nearly white and the cuprous chloride a dull brown.

It is very advantageous to rechlorinate the solution of double chloride copper and potassium after the method of Dr. Sargent, as detailed in e *Journal of the American Chemical Society*, vol. xxii. p. 210. As the lution, however, gradually becomes neutral, we find it desirable to make dition of hydrochloric acid after rechlorinating in sufficient amount to store the original acidity and thus prevent the separation of the salts d increase rapidity of solution. This may readily be done by titrating c.c. of the rechlorinated solution with standard potassium hydrate solun in the cold, taking as the end reaction the point at which the ferric drate formed just fails to go into solution after repeated shaking. tration is then made with 5 c.c. of a solution of one part hydrochloric id to thirteen parts water (the normal acidity of the double chloride lution), with a little neutral ferric solution as indicator. Comparison the acidity of the two solutions with the volume of the solution relorinated will show the amount of hydrochloric acid needed.

As to the accuracy of results, we have checked repeatedly upon various standard steels and have obtained uniform and practically identical results with those obtained by the regular combustion method with platinum tube.

In the above apparatus a number of details have been taken from those presented by Dr. G. W. Sargent, *Journal of the American Chemical Society*, vol. xxii. p. 277, and for these we wish to make hearty acknowledgment.

The Repeated Use of the Double Chloride of Copper and Potassium for the Solution of Steel or Iron in Estimating Carbon.*

In the *Chemical News*, vol. lxxix. p. 169, which appeared April 14 of last year, there is an article headed "The Estimation of Carbon in Steel; Apparatus and Materials," signed J. T., in the course of which it is stated that the copper-ammonium chloride may be re-used as many as eight times, provided it is oxidized by drawing air through it after each solution, and provided the practice of allowing the sample to dissolve overnight is adopted.

Copper-potassium chloride, owing to its freedom from organic matter, has supplanted the ammonium salt. Most chemists use the former in a hydrochloric acid solution, when, by the aid of a stirring machine, the drillings are dissolved in less than an hour. The reaction is expressed in the following equation:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2.$$

If now the cuprous chloride be oxidized to cupric, there is no reason why the double chloride solution should not be used repeatedly until the accumulated iron salts become too great. As stated above, this has been done, but the time consumed in oxidizing by a current of air was too long: several days of an almost continuous current of air through a litre of the acid double chloride failed to completely oxidize the copper salt. The source of my air-current was a filter-pump, making the waste of water very considerable. Therefore, I decided to try the effect of chlorinating the solution direct.

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* George W. Sargent, of the Carpenter Steel Company, Reading, Pennsylvania, in the Journal of the American Chemical Society, xxii. 210.

The result has been most agreeable. At the present time we have three bottles of three quarts' capacity; in one, the filtered double chloride ready for the solution of the drillings is kept; the second receives the undiluted filtrate from the carbon; while the third, filled with the filtrates, stands in the corner of the hood with a current of chlorine gas passing through it. It requires just a day to chlorinate three quarts, and that is about the amount consumed each day. When chlorinated the solution, instead of being of a dirty brown, has almost the original color of copper-potassium chloride. After standing overnight in the hood and being filtered, the objectionable odor of chlorine is gone and the solution is again ready for use. The chlorinated double chloride is more energetic in its solvent action. In some instances the solution of the drillings has been accomplished in fifteen minutes.

As many as eleven solutions have been made with one quantity of the double chloride, and the time required for the eleventh solution and filtration was very little longer than for the first.

The saving effected by re-using the copper-potassium chloride solution is no inconsiderable amount, especially where much of the salt is used. Roughly estimating, one pound of black oxide of manganese and one and a half pounds of hydrochloric acid are sufficient to reconvert three quarts of the double chloride, worth about one dollar.

2. Solution in Cupric Chloride, and Combustion of the Residue.

The only disadvantage in the use of this reagent is the length of time required to dissolve a sample of steel in it. Even with a strongly acid solution and constant stirring, unless the sample is very finely divided, it may require several days for its complete solution.

3. Solution in Iodine or Bromine, and Combustion with Lead Chromate, or Weighing, of the Residue.

The determination by this method, when iodine is used, is carried out exactly as directed for the estimation of "Slag and Oxides," page 78, the residue being filtered on asbestos, dried, and burned with lead chromate or cupric oxide, as directed in A. 2, page 129 *et seq.*

The residue may also be filtered on a counterpoised filter* or a Gooch crucible, washed, dried at 100° C., weighed, the carbonaceous matter burned off, and the residue weighed. The difference between the weights is the amount of carbonaceous matter, which contains, according to Eggertz,† 59 per cent. of carbon. It also contains about 16 per cent. of iodine, so that the residue cannot be burned in a current of oxygen, nor with chromic and sulphuric acids. If bromine is used instead of iodine, great care must be taken in adding the bromine,—10 c.c. bromine for 5 grammes of iron or steel,—as the action is very violent, and, unless the bromine is added very slowly and the solution kept as near 0° C. as possible, there will be oxidation, and, consequently, loss of carbon. The details of the method when bromine is used are otherwise the same as when iodine is the solvent.

4. Solution by Fused Silver Chloride, and Combustion of the Residue.

Fuse in a porcelain crucible 20 grammes of silver chloride, and see that the button when cold has a smooth, flat surface on top. Place the button in a porcelain dish about 6 inches (15 cm.) in diameter, and pour on it 3 grammes of drillings. Add 300 c.c. cold distilled water containing 2 drops of hydrochloric acid, place the dish on a ground-glass plate, and cover it with a bell-glass to exclude the air during the time occupied in dissolving the sample. It is not necessary that the sample should be in drillings, as a single piece will be dissolved in this way. The silver chloride should weigh at least six times as much as the sample of iron or steel. The reaction is a simple substitution by galvanic action, $Fe + 2AgCl = FeCl_2 + 2Ag$, but secondary reactions occur, including the decomposition of water, both hydrogen and oxygen being taken up by the carbon at the moment of its liberation. A slight excess of oxygen over the amount necessary to form water with the hydrogen is taken up and a little hydrogen liberated. There is a tendency, of course, of the ferrous chloride when formed to oxidize, consequently the air must be excluded. The decomposition requires several days, as many as ten if the sample of steel or iron is in a single piece and not very thin. The metallic silver is quite cohesive, and is readily separated from the carbonaceous residue. When the action is finished, remove the mass of silver, washing off any of the carbonaceous matter adhering to it, add a little hydrochloric acid to dissolve any ferric oxide which may have formed, filter, and burn the carbonaceous matter by one of the methods previously described.

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* See page 28.

† Percy, Iron and Steel, page 891.

5. Solution of the Iron in Cupric Sulphate, Filtration, and Combustion of the Residue in a Boat in a Current of Oxygen.

To 3 grammes of steel in a 400 c.c. beaker add 150 c.c. of solution of cupric sulphate, made by dissolving 200 grammes of the copper salt in water, adding a dilute solution of caustic soda until a slight permanent precipitate appears, allowing it to settle, filtering through asbestos, and diluting to 1 litre. For pig-iron, spiegel, and ferro-manganese, use 1 gramme, and 50 c.c. of cupric sulphate solution. Heat the solution gently, and stir well until decomposition is complete. Filter in a glass filtering-tube on asbestos, as described on page 156. Wash well with water, transfer to a boat, as directed on page 157, dry, and burn in a porcelain tube, as directed for A. 1, page 128. The results are apt to be a little low, owing to the difficulty of thoroughly oxidizing the mass of copper mixed with the carbonaceous matter.*

Instead of filtering off the mass of copper, carbonaceous matter, etc., decant the clear supernatant fluid through the filtering-tube, wash several times by decantation, and then dissolve the copper in potassium-cupric chloride, cupric chloride, or ferric chloride. Filter, wash the residue with a little dilute hydrochloric acid, and then with cold water, transfer to a boat, and burn as directed on page 142 *et seq.*

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* See report of the U. S. Board appointed to test iron, steel, and other metals, i. 284.

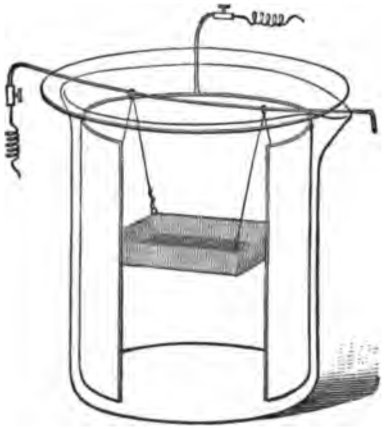
6. Solution of the Iron in Cupric Sulphate, and Oxidation of the Residue by Chromic and Sulphuric Acids.

Treat the sample with solution of cupric sulphate, as in the method just described. Allow the precipitated copper and carbonaceous matter to settle, pour off the clear supernatant liquid, and transfer the residue to the flask A (Fig. 79, page 159) by means of a platinum spatula and a fine jet of water. The water used should not exceed 20 or 25 c.c.* The apparatus is that sketched in Fig. 79, the only difference being that the tube O contains merely a little strong sulphuric acid. Effect the combustion exactly as described on page 158.

7. Solution in Dilute Hydrochloric Acid by the Aid of an Electric Current, and Combustion of the Residue.

The arrangement shown in Fig. 81 may be used in carrying out the details of this method. It consists of a 400 c.c. beaker, in which is a piece of platinum-foil, the wire from which connects with the negative pole of the battery; a small basket of very fine platinum gauze is supported from a platinum wire, on one end of which is a clamp connecting with the positive pole of the battery. The battery is usually a single Bunsen or Grove element, and the intensity of the current should be regulated by varying the distance between the foil and the basket, or by introducing resistance-coils in the connections, so that no gas is given off from the iron. Hydrogen, of course, is given off abundantly from the surface of the foil, and the iron dissolves in the acid as ferrous chloride.

FIG. 81.



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* The borings may be treated with the cupric sulphate solution in the flask A, and the clear liquid drawn off with a pipette. This will avoid the necessity for transferring the residue.

Place in the basket from 1 to 5 grammes of the sample, which should be in pieces and not in powder. Suspend the basket from the wire, having previously connected the rest of the apparatus and poured into the beaker a mixture of 200 c.c. water and 50 c.c. hydrochloric acid, and regulate the intensity of the current as directed above. When solution is complete, remove the foil from the liquid, wash the carbonaceous matter from the basket with a jet of cold water, and determine the amount of carbon by one of the methods previously given.

DETERMINATION OF GRAPHITIC CARBON.

Karsten gave the first information in regard to the existence of graphite in pig-iron, and he suggested dissolving the sample in nitric acid with the addition of a few drops of hydrochloric acid, in hydrochloric acid alone, or in dilute sulphuric acid, boiling the residue with caustic potash, filtering, washing again with hydrochloric acid, and finally with water, and weighing the residue as graphite. A very interesting comparison of the results obtained by the use of different solvents is given by Drown,* and many experiments seem to show that the amount of graphite found varies with the different acids used to dissolve the sample, and also with the variations of treatment when the same acid is used. The usual method is as follows. Treat 1 gramme of pig-iron or 10 grammes of steel with an excess of hydrochloric acid (1.1 sp. gr.). When all the iron is dissolved, boil for a few minutes, allow the graphite to settle, and decant the supernatant fluid on an asbestos filter, using either the perforated boat, Fig. 70, or the filtering-tube, Figs. 74 and 75. Wash several times with hot water by decantation, then pour on the residue in the beaker 30 c.c. of a solution of caustic potash (sp. gr. 1.1), and, when the effervescence ceases, heat the solution to boiling. Filter on the same filter, transfer the graphite etc., to the filter, wash with hot water again, and finally with alcohol and ether. Burn the graphite by one of the methods given under "Determination of Total Carbon," and from the weight of carbonic acid obtained calculate the percentage of carbon existing as *graphite*.

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* Trans. Inst. Min. Engineers, iii. 42.

It frequently happens, when the sample is a high steel, that the residue which remains after treating it as above is black, and contains carbon, but it is not crystalline in appearance, and bears no resemblance to graphite. The same steel will dissolve completely in nitric acid, and when filtered will not leave a trace of carbon on the felt. Steels containing graphite give appreciably less carbon when dissolved in nitric acid than when dissolved in hydrochloric acid. The method giving probably the most accurate and certainly the most uniform results is as follows. Dissolve the weighed sample in nitric acid (sp. gr. 1.2), using 15 c.c. of acid to each gramme taken for analysis. Filter on the perforated boat or on an ignited asbestos filter, in a glass tube, transfer the residue to the filter, and wash thoroughly with hot water. Treat the residue on the filter with hot caustic potash solution, 1.1 sp. gr. (as the silicon is all oxidized to silica there will be no effervescence), wash thoroughly with hot water, then with a little dilute hydrochloric acid, and finally with hot water. Burn the carbon by one of the methods previously mentioned and calculate the carbonic acid obtained to carbon, and call the result *graphite.**

DETERMINATION OF COMBINED CARBON.

Indirect Method.

Having determined the total carbon and the graphite, by subtracting the latter from the former we obtain the amount of carbon existing in the *combined condition.*

Direct Method.

This method was first introduced by Eggertz† in 1862. It is based on the fact that when steel containing carbon is dissolved in nitric acid (1.2 sp. gr.), the carbon, which sometimes at first separates out in flocks of a brownish color, is eventually dissolved, giving to the solution a depth of color directly proportionate to the amount of combined carbon in the steel. To use this in practice it is only necessary to determine accurately the amount of combined carbon contained in a steel, by a combustion method, and to compare the depth of color in a solution of this standard with that of any unknown steel, in order to ascertain the amount of carbon in the latter. There is, however, a limitation to the application of this method. Reference was made on page 126 to the fact that combined carbon is now believed to exist in two conditions in steel, or rather that under certain circumstances a portion of the combined carbon changes its condition, and, from a chemical point of view, while it is still combined carbon, in that it is soluble in nitric acid, it fails to impart so dark a color to its nitric acid solution as it did in its original state. The circumstances under which a change of this kind occurs are quite well known, and are merely those occasioned by the mechanical treatment to which steel is submitted, such as hammering, rolling, hardening, tempering, etc.* It may be stated, then, as a general proposition, that *the standard steel for the color-test should be of the same kind and in the same physical condition as the samples to be tested.*

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* Shimer (Jour. Amer. Chem. Soc., xvii. 873) has shown that titanium carbide is insoluble in dilute hydrochloric acid and that the nitric acid method is the only accurate one for the determination of graphite.

† Jern-Kontorets Annaler, 1862, p. 54; 1874, p. 176; 1881, p. 301; Chem. News, vii. 254; xliv. 173.

To obtain the best results samples should be taken from the original ingots which have not been reheated, rolled, or hammered; Bessemer steel should be compared with Bessemer, crucible with crucible, open hearth with open hearth; the standard should contain approximately the same amount of carbon as the samples to be tested, and should have as nearly as possible the same chemical composition. The only elements that seem to have any decided effect on the color of the nitric acid solution are copper, cobalt, and chromium.

Weigh out carefully .2 gramme of each sample, including the standard, into test-tubes 6 inches (150 mm.) long and ⅝ inch (16 mm.) in diameter. The test-tubes should be perfectly clean and dry, and each one marked with the number of the sample on a small gummed label near the top. A little wooden rack (Fig. 82) is convenient for holding the test-tubes in the weighing-room, and to avoid all chance of error the tube is not placed in the rack until the sample has been weighed and is ready to be transferred. A little platinum or aluminum dish about 1½ inches (40 mm.) in diameter, with a spout, and furnished with a counterpoise (Fig. 44, page 36), is very convenient for holding the drillings, which are brushed from it into the test-tube with a camel's-hair brush. A very excellent form of water-bath is shown in Fig. 83. It may be provided with a constant level arrangement, consisting of a tubulated bottle, the height of the end *b* of the vertical tube *a* fixing the level of the water in the bath. A is the bath and B the rack.

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* Two very interesting papers on this subject will be found in the Chem. News, J. S. Parker, "On the Varying Condition of Carbon in Steel," xlii. 88; T. W. Hogg, "On the Condition of Carbon in Steel," xlii. 130.

FIG. 82.

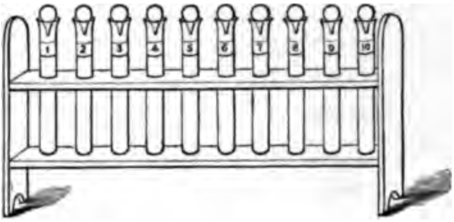
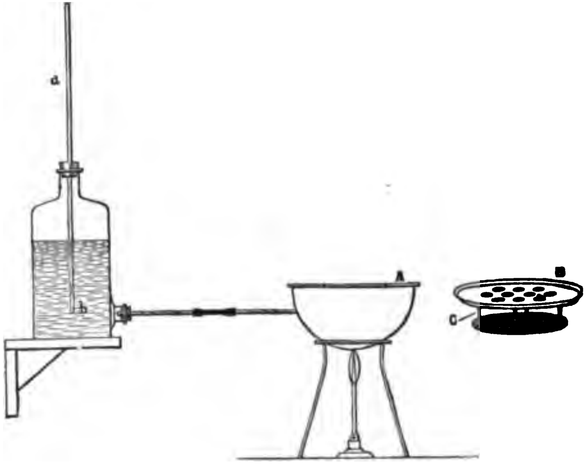


FIG. 83.

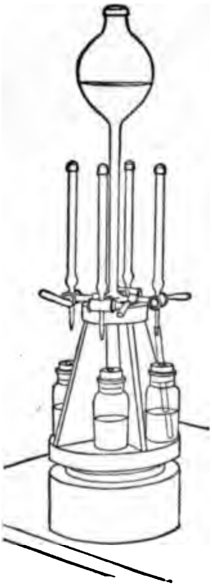


The top of the rack is of sheet-copper, perforated to receive the test-tubes, the bottoms of which rest on the coarse copper gauze, which is joined to the top by the uprights C. The top of the rack rests on a flange around the top of the bath.

Place the test-tubes in the rack B, and stand the rack in the bath ich contains cold water. Drop into each test-tube, from a pipette, the per amount of nitric acid (sp. gr. 1.2). For steels containing less than per cent. carbon use 3 c.c. nitric acid; from .3 to .5 per cent. carbon, c.c.; from .5 to .8 per cent., 5 c.c.; from .8 to 1 per cent., 6 c.c.; and er 1 per cent., 7 c.c. An insufficient amount of acid gives the solution slightly darker tint than it should properly have.

The apparatus shown in Fig. 84* is useful for the rapid addition of easured quantities of nitric acid to the samples.

FIG. 84.



It consists of a glass reservoir holding 750 c.c., communicating below th four burettes graduated to *deliver* various quan- ies of acid up to 10 c.c. Each burette is furnished ith a loose-fitting glass cap. The burettes are fitted th three-way glass stopcocks, so that a quarter of revolution connects them with the reservoir, and hen the proper amount of acid has run in, the stop- ck is turned another quarter, which shuts off the servoir and completely empties the burette, thus de- ering the exact amount of acid measured into the st-tube containing the weighed sample of steel in hich carbon is to be determined.

As shown in the cut, each test-tube stands in a ttle of cold water to prevent too violent action of the id during solution. The whole apparatus is mounted a rotary stand, and, as used at the laboratory of the thlehem Iron Company, is contained in a small hood ar the drill and balance described on page 16, so at the operator, seated on a revolving stool, can add acid to one sam- of steel while the drillings of the next sample are falling into the lance-pan.

The apparatus, as here shown, is a modification by Mr. Albert L. lby, of the Bethlehem Iron Company, of an apparatus first designed Mr. E. A. Uehling in 1884.

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* Communicated to the author.

The nitric acid is made by adding its own volume of water to acid of the usual strength (1.4 sp. gr.). It should be absolutely free from chlorine or hydrochloric acid, as, according to Eggertz, .0001 gramme chlorine in a nitric acid solution of .1 gramme iron in 2.5 c.c. nitric acid gives a decidedly yellow color. The nitric acid should be added slowly, to prevent violent action, and the drillings should not be too fine, for the same reason. Place in the top of each test-tube a small glass bulb* or a very small funnel, heat the water in the bath to boiling, and boil until all the carbonaceous matter is dissolved, shaking the tubes from time to time to prevent the formation of a film of oxide. The time required for solution is for low steels about twenty minutes and for high steels (over 1 per cent. carbon) forty-five minutes. After entire solution of the carbonaceous matter, prolonged heating tends to make the color lighter; therefore, as soon as the absence of small bubbles and the disappearance of any brownish flocculent matter show complete solution, remove the rack from the bath and stand it in a dish of cold water. The dish should be about the same size as the bath, so that the top will be covered by the top of the rack, thus excluding the light from the solutions, in which case the color will not fade for a long time. Under all circumstances the solutions should be kept out of the light, and especially out of direct sunlight, as much as possible. If there should be necessarily, in the steels operated on at one time, a wide range in carbon, the test-tubes should be removed from the bath as fast as their respective contents are dissolved and placed in cold water in a dark place. The appearance of the drillings will often give an idea of the approximate carbon contents of a sample, but when there is no clue whatever, it is best to begin by adding 3 c.c. nitric acid to the weighed portion in the test-tube, and increase the amount 1 c.c. at a time as the depth of color of the solution or the amount of flocculent carbonaceous matter indicates a higher carbon percentage. To compare the colors of tions, pour the standard into one of the carbon tubes (Fig. 85), ut the test-tube with a little cold water, add it to the solution arbon tube, and dilute to a convenient amount.

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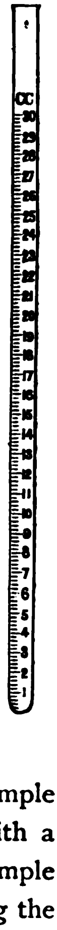
* These bulbs are easily made by sealing one end of a glass tube in the blow-pipe flame, heating it, blowing a bulb of the proper size, allowing it to cool, heating it above the neck, and drawing it out as shown in Fig. 82.

FIG. 85.



dilution should be sufficient to make the volume of the standard at least twice as great as the volume of acid y used to dissolve the sample, as this amount of water sary to destroy the color due to the ferric nitrate. It not, however, greatly exceed this amount, and should be nvenient multiple of the carbon contents of the standard s of a per cent. Thus, if a standard contains .45 per bon, dilute the solution in the carbon tube to 9 c.c., then . will equal .05 per cent. The carbon tubes should be (12 mm.) in diameter, holding at least 30 c.c., and grad- $\frac{1}{10}$ c.c. The tubes should have exactly the same diam- d the glass should be perfectly colorless and have walls same thickness. They should, of course, be most ly graduated.

E. F. Wood,* of the Homestead Works, leaves the lower the tubes free from graduations to give a clear space for ng the colors. He considers this especially necessary in ls, for which he uses 1 gramme of the sample, dissolves c. of nitric acid, boils for from five to seven minutes in a e bath at 140° C., and compares in tubes ¾ inch (18 mm.) eter.

standard having been prepared, pour the solution of the sample sted into another carbon tube, rinse the test-tube into it with a d water, and compare the colors. If the solution of the sample r than that of the standard, add water little by little, shaking the ll to mix the solution until the shades are exactly the same. minute or two for the solution to run down the walls of the d read the volume. If the standard was diluted as above, then, e, each c.c. will equal .05 per cent. carbon, and if the volume of the sample is 10.5 c.c. it will contain .525 per cent. carbon. If the solution of the sample when first transferred to the tube should be lighter in color than the standard, a lower standard must be used, or this one may be diluted to, say, 13.5 c.c., in which case the number of c.c. divided by 3 will give the percentage of carbon in tenths. The color may be compared by holding the two tubes in front of a piece of white paper held towards the light, but a camera made of light wood and blackened inside is most convenient, and at night is quite invaluable. It is shown in Fig. 86, and consists of a box 3½ inches (90 mm.) high inside, 1½ inches (38 mm.) wide at one end, and 5 inches (127 mm.) at the other. It is 24 inches (610 mm.) long, and is supported on a rod, which can be raised and lowered to suit the convenience of the observer. The small end is closed by a piece of ground glass, which slides in through a slot on top 1 inch (25 mm.) from the end. Immediately beyond this is another slot to receive a thin piece of faintly blue glass, which is inserted when the tests are made at night, using an oil-lamp placed on a stand just beyond the camera. In fact, in many steel-works, to avoid the differences between the colors as seen by daylight and lamplight, *all* comparisons are made in a dark room, using a box or camera and an oil-lamp. Two holes in the top of the camera just inside the ground-glass screen receive the carbon tubes, the ends of which rest on a piece of black cloth on the bottom of the camera inside. Another piece of black cloth fastened across the top of the camera, covering the top of the ground-glass slide, and having holes just large enough to admit the tubes, excludes all light except that at the back of the tubes. A north light is much the best for comparing the colors, and, as to most observers the left-hand tube appears a little the darker, the color will be exactly matched when, the tubes being

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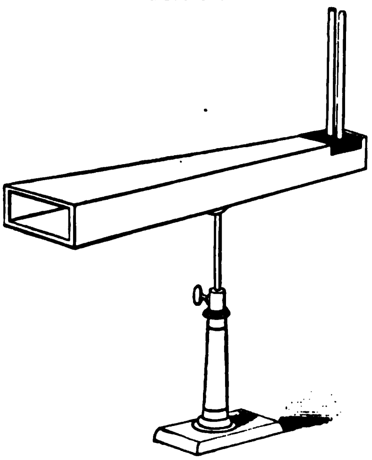
* Communicated to the author.

FIG. 86.



reversed, the left-hand tube still appears a little the darker of the two.

Instead of diluting the solutions to agree with a standard, as above described, some chemists use a rack of permanent standards, as suggested by Britton.* The principal difficulty heretofore attending the use of permanent standards has been the impossibility of preventing their fading; but, according to Eggertz,† this is now entirely overcome by the method of preparing them suggested by Prof. F. L. Ekman. The details are as follows. Dissolve 3 grammes of neutral ferric chloride in 100 c.c. water containing 1.5 c.c. hydrochloric acid; dissolve 2.1 grammes cupric chloride in 100 c.c. water containing .5 c.c. hydrochloric acid, dissolve 2.1 grammes cobaltic chloride in 100 c.c. water containing 5 c.c. hydrochloric acid, using the neutral salts in all cases. These solutions will contain about .01 gramme of the metal to the c.c., and by adding to 8 c.c. of the iron solution 6 c.c. of the cobalt solution, 3 c.c. of the copper solution, and 5 c.c. water containing .5 per cent. hydrochloric acid, a liquid is obtained which has a color approximating that obtained by dissolving .2 gramme of steel, containing 1 per cent. of carbon, in nitric acid, and diluting to 10 c.c., or .1 per cent. carbon to the c.c. Prepare a number of test-tubes of the size described on page 171, but in this case it is essential that they should be of exactly the same diameter, and that the glass should be as nearly colorless as possible. By successive dilutions with water containing .5 per cent. hydrochloric acid, of the normal solution prepared as above, make solutions of about the proper strength for the series required.

The variations should be about .02 per cent. between the different tubes of the series, corresponding to, say, the even hundredths. There should be about 10 c.c. of solution in each tube, and then the color of each should be compared with a standard steel, diluted to the exact strength required in the permanent standard. For example, if the standard steel contains .4 per cent. carbon, and you wish to get the exact color for the .32 per cent. carbon tube in the permanent series, dissolve .2

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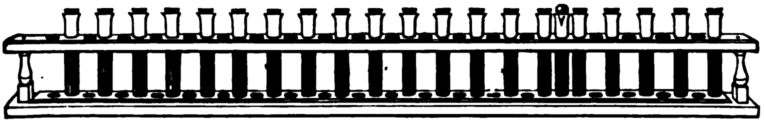
* Chem. News, xxii. 101.

† Ibid., xliv. 173.

gramme of the standard exactly as directed on page 173, pour the solution into a carbon tube, and dilute it in accordance with the formula, carbon required : carbon of standard :: 10 c.c. : the number of c.c. required, or, in this case, 32 : 40 :: 10 c.c. : 12.5 c.c. Therefore dilute the solution in the carbon tube to 12.5 c.c., pour 10 c.c. into a test-tube exactly like those used for the permanent standards, and compare it with the .32 per cent. carbon tube. If the color of the permanent solution is not exactly the same, correct it by adding portions of the solutions of the iron, cobalt, or copper salts, or water containing .5 per cent. hydrochloric acid. The iron salt or hydrochloric acid alone gives a yellowish, the cobalt salt a brownish, and the copper salt a greenish, tone to the solution. The standards may now be arranged in a rack, as shown in Fig. 87. The colors of the permanent standards once fixed, the samples to be analyzed are treated exactly as described on page 173, the test-tubes used being precisely like those containing the permanent standards, and each one carefully graduated to contain 10 c.c. When the samples (.2 gramme each) are dissolved and cooled, dilute each solution in turn with cold water to 10 c.c., mix thoroughly, and compare it with the standards in the rack, by which means the carbon may be estimated to the nearest hundredth of a per cent.

FIG. 87.



In testing white cast iron, use only .05 gramme, dissolve in 7 c.c. nitric acid, dilute the standard to some convenient amount approximating 20 c.c., and compare as quickly as possible to avoid the precipitation of carbonaceous matter, which is apt to occur under these circumstances. The graphite in ordinary gray pig-iron, and sometimes even in steels, renders filtration necessary. In this case add to the cold acid solution one-half of its volume of water, filter through a small, dry, ashless filter into the carbon tube, wash with as little water as possible, and compare as usual.

DETERMINATION OF TITANIUM.

By Precipitation.

Only traces or very minute amounts of titanium are found in steel, but notable quantities exist in some kinds of pig-iron. As pointed out by Riley,* when pig-iron containing titanium is dissolved in hydrochloric acid a portion of the titanium goes into solution, while the remainder is found with the insoluble matter. The insoluble portion, as noticed on page 85 *et seq.*, contains phosphoric acid. It is a curious fact that as titanic acid interferes with the determination of phosphoric acid by its tendency to form upon evaporation to dryness an insoluble phospho-titanate, so phosphoric acid interferes with the determination of titanic acid by partially preventing the precipitation of titanic acid from its boiling sulphuric acid solution. The best method, therefore, for the determination of titanium is to proceed exactly as for the determination of phosphorus when titanium is present, as directed on page 85 *et seq.*, until the residue from the aqueous solution of the sodium carbonate fusion is obtained. Dry this residue, transfer it to a large platinum crucible, preferably the one in which the sodium carbonate fusion was made, burn the filter, add its ash to the residue, and fuse the whole with fifteen or twenty times its weight of potassium bisulphate. In fusing with potassium bisulphate it is necessary to begin with a very low heat, and to raise the temperature very slowly and carefully to a low red heat, as the mixture has a strong tendency to boil over the top of the crucible whenever the temperature is increased too rapidly. When the lid of the crucible is raised, fumes of sulphuric anhydride should come off, and the fusion should be kept at this point for several hours, or until it is quite clear and the whole of the ferric oxide has been dissolved. Allow the fused mass to cool, add to it from 10 c.c. to 20 c.c. of strong sulphuric acid, and heat until it is perfectly liquid. When cold it will remain liquid. Pour it carefully into 400 c.c. of cold water in a 600 c.c. beaker. Add a little hydrochloric acid if necessary and 50 c.c. of strong sulphurous acid, or 5 c.c. of ammonium bisulphite. Filter into an 800 c.c. beaker, add ammonia until a permanent precipitate forms, redissolve with a few drops of hydrochloric acid, add a filtered solution of 20 grammes of sodium acetate and one-sixth the volume of the solution of acetic acid (1.04 sp. gr.), and heat to boiling. The titanic acid is precipitated almost immediately in a flocculent condition and quite free from iron. Boil for a few minutes, allow the titanic acid to settle, filter, wash with hot water containing a little acetic acid, dry, ignite, and weigh as titanic acid, which contains 60 per cent. titanium. Should the precipitate contain any appreciable amount of ferric oxide, fuse with bisulphate and reprecipitate in the same way.

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* Jour. Chem. Soc., xvi. 387.

By Volatilization.

Drown * suggested the method of determining titanium by volatilizing it in a current of chlorine gas. The details, with some modifications, are as follows. Treat the sample exactly as directed for the determination of silicon, *by volatilization in a current of chlorine gas*, page 73 *et seq.*

To the filtrate from the silica (page 77) add a slight excess of ammonia, acidulate with acetic acid, boil, filter, wash, and ignite the precipitate. As this precipitate may contain a little ferric oxide (carried over mechanically as ferric chloride), phosphoric acid, tungstic acid, etc., fuse it with a little sodium carbonate, dissolve the fused mass in hot water, filter, wash, dry, and ignite the residue, which will contain all the titanic acid as sodium titanate, and any iron that may have been present as ferric oxide. The filtrate will contain the phosphoric acid, etc. Fuse the ignited residue with a little potassium bisulphate, treat it in the crucible with strong sulphuric acid, as directed on page 179, and determine the titanic acid in the manner there described.

DETERMINATION OF COPPER.

For the determination of copper the precipitate by hydrogen sulphide, obtained in the determination of phosphorus (page 82), may be used, but in this case the precipitate must be filtered off before getting rid of the excess of hydrogen sulphide, after which, if any additional precipitate of arsenious sulphide is thrown down in the filtrate, it must be filtered off before proceeding with the determination of phosphorus. Dry and ignite the filter with the precipitate of copper sulphide, etc., in a porcelain crucible, burn off all the carbon from the paper, allow the crucible to cool, and digest the precipitate at a gentle heat with nitric acid and a few drops of sulphuric acid, keeping the crucible covered with a small watch-glass. When the copper sulphide is entirely dissolved, remove the watch-glass and evaporate the solution until all the nitric acid is expelled and fumes of sulphuric anhydride are given off. Allow it to cool, add enough water to dissolve all the cupric sulphate, heating gently, if necessary, and wash the solution into a platinum crucible. Place the crucible in the little brass holder (Fig. 88), attach the weighed platinum cylinder, and connect the battery. The battery should consist of three Daniell's two-quart cells, arranged as shown in Fig. 89. The connectors *a*, *b* pass through the sides of the box (which should be covered), and, the jars being connected as shown in the sketch, by simply changing the wire from *a* to *b*, three cells are brought into action instead of two. For depositing the small amount of copper found in iron or steel, two cells furnish a sufficiently strong current. The platinum cylinder should weigh about 3 or 4 grammes;

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* Trans. Inst. Min. Engineers, viii. 508.

Fig. 88.

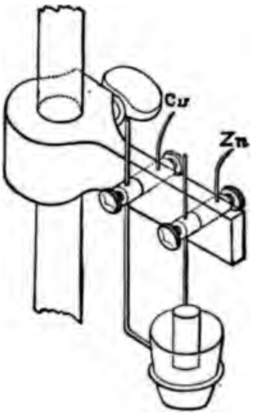
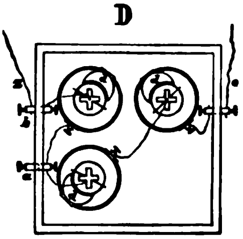


Fig. 89.



it is lowered into the liquid until it is just clear of the bottom of the crucible, and the crucible is covered with two small pieces of glass to prevent the liquid being carried off by the escaping gas. It is much neater to deposit the copper on the cylinder than in the crucible, as it weighs less, is quite as easy to wash and dry, and there is no danger of any silica or dirt from the solution being covered by the deposited copper. When the copper is all deposited, usually in two or three hours, remove the cylinder, wash it with cold water, then with alcohol, dry at 100° C., cool, and weigh. The increase of weight is copper.

In pig-irons containing titanium it is necessary to use a separate portion for the determination of copper. In steels, the solution in the flask from the determination of sulphur (page 60) may be used for the determination of copper. In this case, wash the contents of the flask into an 800 c.c. beaker, nearly neutralize with ammonia, add 5 c.c. hydrochloric acid, heat the solution to boiling, and pass hydrogen sulphide through the boiling solution for fifteen or twenty minutes, filter, wash with hot water, and treat the precipitate as directed above. In the case of pig-irons, however, it is best to dissolve in aqua regia, evaporate to dryness, redissolve in hydrochloric acid, filter, reduce the iron in the filtrate with ammonium bisulphite, boil off the excess of sulphurous acid, and precipitate by hydrogen sulphide. Instead of using hydrogen sulphide, the copper may be precipitated in a sulphuric acid solution by sodium hyposulphite. Dissolve 5 grammes of the sample in a mixture of 150 c.c. water and 12 c.c. strong sulphuric acid. Dilute to about 500 c.c. with hot water, heat to boiling, and add 3 grammes of sodium hyposulphite dissolved in 10 c.c. hot water. Boil for a few minutes, allow the precipitate to settle, filter, and wash with hot water. Dry the precipitate, which, besides the cupric sulphide, may consist of graphite, silica, etc.; transfer it to a small beaker, burn the filter, and add the ash to the main portion. Digest the whole with aqua regia, dilute with hot water, filter, wash, add a few drops of sulphuric acid, and evaporate until fumes of sulphuric anhydride are given off, cool, dissolve in water, transfer to the platinum crucible, and determine the copper by the battery as directed above.

Instead of determining the copper by electrolysis, it may be determined as cuprous sulphide, Cu_2S, or as oxide, CuO. To determine it as cuprous sulphide, dilute the sulphate obtained by any of the methods mentioned above with water to about 50 c.c., add an excess of ammonia, filter from ferric oxide, etc., wash with ammoniacal water, and pass hydrogen sulphide through the cold solution. Filter, wash with hydrogen sulphide water, dry the filter and precipitate, transfer the latter to a small porcelain crucible, burn the filter, and add its ash to the precipitate. Add to the precipitate in the crucible about twice its volume of flowers of sulphur and ignite it in a current of hydrogen, as directed for the determination of manganese as MnS, page 112. Weigh as cuprous sulphide, which contains 79.82 per cent. copper.

Instead of igniting the precipitate obtained above as cuprous sulphide, the copper may be determined as oxide, as follows. Dissolve the sulphide in aqua regia in a small porcelain dish, evaporate nearly dry, dilute with hot water, heat to boiling, and add a slight excess of a dilute solution of caustic soda or potash. Filter on a small ashless filter, wash with hot water, dry, transfer the precipitate to a platinum crucible, burn the filter and add its ash to the precipitate, moisten the whole with nitric acid, and heat very gently at first, but increase the heat slowly to redness. Cool, and weigh as copper oxide, which contains 79.85 per cent. copper.

DETERMINATION OF NICKEL AND COBALT.

The Acetate Method.

Treat 3 grammes of the drillings exactly as directed for the determination of manganese by the acetate method (page 108 *et seq*). The precipitate by hydrogen sulphide (page 110) will contain all the nickel and cobalt and a portion of the copper contained in the sample. Filter this precipitate on a small washed filter, wash with hydrogen sulphide water containing a little free acetic acid, dry and ignite the filter and precipitate, and transfer them to a small beaker. Dissolve in hydrochloric acid with a few drops of nitric acid, evaporate to dryness, redissolve in from 10 to 20 drops of hydrochloric acid, dilute with hot water to about 50 c.c., heat the solution to boiling, and pass a stream of hydrogen sulphide through the boiling solution to precipitate any copper that may be present. Filter, wash with hot water, evaporate the filtrate to dryness, moisten the dry mass with 4 or 5 drops of hydrochloric acid, add 20 or 30 drops of cold water and then 2 or 3 grammes of potassium nitrite (KNO_2) * dissolved in the least possible amount of water and acidulated with acetic acid. The presence of cobalt is shown by the formation of a bright yellow precipitate of potassium-cobalt nitrite, $(KNO_2)_6Co_2(NO_2)_6 + Aq$. Stir the solution, and allow it to stand twenty-four hours, with occasional stirring. Filter on a small ashless filter, wash with water containing potassium acetate and a little free acetic acid, remove the filtrate which contains the nickel, and wash the precipitate and filter free from potassium acetate with alcohol. Ignite the filter and precipitate carefully in a porcelain crucible, being careful not to raise the temperature high enough to fuse the precipitate; transfer to a very small beaker, and digest in hydrochloric acid and a little potassium chlorate. Evaporate to dryness, redissolve in from 3 to 5 drops of hydrochloric acid, dilute with cold water, add about 1 gramme of sodium acetate, and boil for an hour to precipitate the small amount of ferric oxide and alumina that is always present. Filter, to the filtrate add excess of ammonia and ammonium sulphydrate, and heat to boiling. As soon as the precipitate of cobalt sulphide has settled, filter, wash with water containing a little ammonium sulphydrate, dry, and ignite the precipitate and filter in a platinum crucible. When all the carbon is burned, allow the crucible to cool, pour in a little nitric acid, heat carefully, and finally evaporate to dryness. Add a few drops of sulphuric acid, digest until the sulphide and oxide are changed to cobalt sulphate, drive off the excess of sulphuric acid, heat finally to dull redness for a few moments, cool, and weigh as cobalt sulphate, $CoSO_4$, which contains 38.05 per cent. of cobalt. Heat the filtrate from the potassium-cobalt nitrite to boiling, add a slight excess of caustic potash, boil for a few minutes, filter, and wash the precipitate of nickel oxide with hot water. Dissolve the precipitate on the filter with hydrochloric acid, allow the solution to run back into the beaker in which

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See page 47.

: nickel oxide was precipitated, and wash the filter with hot water. raporate the solution to dryness, redissolve in from 3 to 5 drops of hy- ochloric acid, dilute with cold water to about 50 c.c., add 1 gramme sodium acetate, boil for an hour, filter off any ferric oxide and umina, and wash with hot water. To the filtrate add an excess of nmonium sulphydrate (a brown color shows the presence of nickel), idulate with acetic acid, heat to boiling, and pass a current of hydrogen lphide through the boiling solution until the precipitated sulphur and ckel sulphide agglomerate. Filter, wash with hydrogen sulphide water, y, and ignite the filter and precipitate. Allow the crucible to cool, add little ammonium carbonate to the precipitate, heat to dull redness, and latilize any sulphuric acid that may have been formed as ammonium lphate, cool, and weigh as nickel sulphide or nickel oxide, which con- ins 78.55 per cent. of nickel. The nickel and cobalt may also be weighed the metallic condition by precipitating them by the battery from the nmoniacal solutions of the sulphates. If it is not desired to separate em, evaporate the filtrate from the precipitated copper sulphide with an cess of sulphuric acid until the hydrochloric acid is driven off and fumes sulphuric anhydride appear, allow the beaker to cool, add about c.c. water, then an excess of ammonia, filter if necessary, transfer to a itinum crucible, and precipitate on a small cylinder (Fig. 88, page 181) a strongly ammoniacal solution, using three cells of the battery. Wash e cylinder with water, then with alcohol, dry at 100° C., and weigh as ckel and cobalt. To determine the nickel and cobalt separately, precipi- e the cobalt as potassium-cobalt nitrite, treat the ignited cobalt precipi- e with an excess of sulphuric acid, heat until fumes of sulphuric hydride are given off, dilute a little, make the solution strongly ammoni- al, and precipitate the cobalt as above directed. Precipitate the nickel ide, in the filtrate from the cobalt, by caustic potash solution, filter, ish, dissolve on the filter in hydrochloric acid, evaporate the solution th sulphuric acid, add excess of ammonia, and precipitate the nickel by e battery as above.

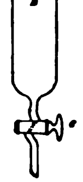
For the analysis of nickel steel, which contains from 2 to 3 per cent. nickel, use 1 gramme of the sample, and, after obtaining the precipitate of nickel sulphide as described above, burn it with the filter in a porcelain crucible, allow it to cool, add a little pure powdered sulphur, and ignite in a stream of hydrogen gas as described on page 112. Weigh as nickel sulphide.

The Ether Method.

This method of separation, due to J. W. Rothe,* is founded on the fact that ether will take from an aqueous hydrochloric acid solution nearly all the ferric chloride, leaving in the solution the chlorides of nickel, cobalt, aluminum, chromium, manganese, and copper. The method was used first in this country by Mr. George H. Chase, of the Midvale Steel Company, and is given in considerable detail by Prof. Ad. Carnot in his "Methodes d'Analyse des Fontes, des Fers, et des Aciers," 1895, p. 123 *et seq.*

Dissolve from 2† to 5 grammes of the drillings in a 250 c.c. beaker in aqua regia. Evaporate to dryness to render silica insoluble, redissolve in hydrochloric acid, dilute slightly, filter, and evaporate the filtrate to syrupy consistency. The success of the separation depends largely upon the specific gravity of the solution, as a solution of the density 1.100 to 1.105 saturated with ether retains the smallest amount of ferric chloride. The tube shown in Fig. 90, suggested by Carnot, is admirably adapted for the treatment with ether. It consists of a bulb, B, of 200 c.c. capacity, about 20 cm. (8 inches) high and 3.5 cm. (1.5 inches) wide, with a tube at either end 3 mm. (1/8 inch) internal diameter, carrying the stopcocks A and C. The upper one connects with a bulb, D, of 100 c.c. capacity, with a mark at *m* to show when the bulb contains 60 c.c.

FIG. 90.



Close both stopcocks, pour a few drops of ether into the upper bulb, open A to allow the ether to run into B. Close A, warm the bulb B with the hand, and open and close C. This will create a partial vacuum in B. Transfer the solution from the beaker to the bulb D, washing it out of the beaker with hydrochloric acid of 1.124 sp. gr. and filling D to the mark *m*. This strength of hydrochloric acid gives the solution, after the separation of the ferric chloride by ether, a sp. gr. of 1.100. Stand the tube in a vessel of cold water, open A and allow the solution to run into B. Close A and fill the bulb D with ether. Allow the ether to flow slowly into B so that it forms a separate layer over the hydrochloric acid solution. Mix the two liquids gradually by giving the apparatus a circular motion, replacing it in the cold water from time to time so as to avoid a rise in the temperature, which would cause a reduction by the ether of some of the ferric chloride. Finally close A, shake the tube well, open A to relieve the pressure, return the tube to the water, and allow it to stand some minutes to give the liquids the opportunity to separate. The upper stratum is the ethereal solution of the ferric chloride and the lower the hydrochloric acid solution of the other metals, with usually about 1 per cent. of the ferric chloride. Open the stopcock C, allow the lower solution to run into a small beaker, close C, and wash the end of the tube with a little water. Introduce about 10 c.c. of hydrochloric acid (1.1 sp. gr.) into the bulb D, allow it to run into B, close A, shake the apparatus and allow it to stand for a few minutes. Allow the lower liquid to run into the beaker, which will now contain all the nickel, cobalt, etc., that were in the steel.* One separation with ether is generally sufficient, but if it is considered desirable to remove still more of the iron, run the solution and washings into the bulb of another tube like the one described instead of into a beaker, and repeat the treatment with ether.

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* Mittheilungen aus den Königlich Tech. Versuchsanstatten zu Berlin, 1892, Part iii.

† For nickel steel containing from 2 per cent. to 3 per cent. of nickel 2 grammes are sufficient.

Heat the solution in the beaker to drive off the ether dissolved in it, add bromine or a little hydrogen peroxide and excess of ammonia, boil, and filter. Redissolve the precipitate and repeat the operation, adding the two filtrates together. The filtrates contain all the nickel, cobalt, and copper, while the insoluble matter contains, besides ferric hydrate, any alumina and chromium sesquioxide that may have been in the steel. Acidulate the filtrate with hydrochloric acid, adding about 5 per cent. of its volume in excess, and precipitate the copper with hydrogen sulphide. Filter and wash. To the filtrate add an excess of ammonia, then a few c.c. of ammonium sulphydrate, acidulate with acetic acid, and pass hydrogen sulphide through the boiling solution. Filter and wash the precipitate of sulphur and nickel and cobalt sulphides. Test the filtrate by adding an excess of ammonia, and if it darkens repeat the precipitation with ammonium sulphydrate, acetic acid, and hydrogen sulphide. In the case of nickel steel, cobalt is generally disregarded, and the precipitate is ignited and weighed after treatment with ammonium carbonate as nickel oxide, NiO.

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* To recover the ether, dilute it in the tube with an equal volume of water, shake the tube and allow it to stand. The ether rises to the top and the aqueous ferric chloride solution remains below. Draw off the latter and distil the ether from caustic lime.

Or, heat the liquid separated from the ethereal solution to drive off the ether, dilute slightly, pass hydrogen sulphide to precipitate the copper, filter, and wash. Heat the filtrate to drive off the hydrogen sulphide, add 10 c.c. of strong sulphuric acid and a little nitric acid, and evaporate until fumes of sulphuric anhydride are given off. Cool, dilute to 50 c.c., add ammonia in excess, boil, and filter. Redissolve the precipitate in dilute sulphuric acid, reprecipitate, and filter. Add the filtrates together and precipitate on the battery as metallic nickel.

To separate the nickel and cobalt, dissolve the ignited precipitate of the sulphide obtained above in hydrochloric acid with a little nitric acid, evaporate to very small bulk, and separate with potassium nitrite as described on page 184.

DETERMINATION OF CHROMIUM.

All chrome steels are soluble in hydrochloric acid or in aqua regia, leaving occasionally a residue which may contain small amounts of chromium. For gravimetric determinations a preliminary separation of the greater part of the iron is practically a necessity, and Rothe's method for accomplishing this is unequalled both for accuracy and speed.

The Ether Method.

Treat from 1 to 5 grammes of the steel exactly as described for the determination of nickel by the ether method (page 186), until the precipitate by ammonia, consisting of ferric oxide, chromium sesquioxide, and manganese oxide, is obtained. In the absence of nickel a single precipitation is sufficient; in the event of its being present, two or even three precipitations may be necessary, and of course the chromium and nickel may be determined at the same time. Dry the precipitate, ignite and fuse it with sodium carbonate and a little sodium nitrate. Extract the fused mass with water, filter, and wash with water containing a little sodium carbonate. The filtrate contains the chromium as sodium chromate, part of the alumina, and part of the manganese. The insoluble matter consists of ferric oxide and the rest of the alumina and manganese. Evaporate the filtrate with an excess of ammonium nitrate, adding ammonia from time to time until the solution becomes syrupy. Dilute, and filter from the alumina and manganese. To the filtrate, after boiling off the ammonia, add an excess of sulphurous acid, boil until it no longer smells of sulphurous acid, add ammonia in excess, boil, filter, and wash the precipitate of chromium sesquioxide. Dissolve in a little hydrochloric acid, reprecipitate with ammonia, filter, wash, ignite, and weigh as chromium sesquioxide, which contains 68.48 per cent. of chromium.

The Volumetric Method.

Galbraith * has suggested a rapid method for the determination of chromium when it is present in appreciable amounts, as in chrome steel or chrome pig-iron. Dissolve from 1 to 3 grammes of the sample in dilute sulphuric acid (1 part sulphuric acid and 6 parts water), add potassium permanganate in crystals until the iron is all oxidized and the liquid is quite red in color, then add as much more to oxidize the chromium to chromic acid. Heat the solution to boiling, and boil until the permanganate is all decomposed and there remains a precipitate of manganese

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* Chem. News, xxxv. 151.

oxide. Filter, wash with hot water, to the filtrate add a measured volume of standardized ferrous sulphate, and determine the excess of ferrous sulphate by a standard solution of permanganate. From the amount of ferrous sulphate oxidized by the chromic acid calculate the amount of chromium. The reaction is $6FeSO_4 + 2CrO_3 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6H_2O$, or 1 equivalent of chromic acid will oxidize 3 equivalents of ferrous sulphate to ferric sulphate. Therefore, if the value of the permanganate is known in metallic iron, and consequently the value of the ferrous sulphate (it being standardized by the permanganate) in metallic iron, the amount of chromium is calculated as follows: 3 equiv. Iron = 168 : 1 equiv. Chromium = 52.14 : : the value of the ferrous sulphate oxidized by the chromic acid in iron : its value in chromium; or multiply the value of the ferrous sulphate oxidized, in iron, by $\frac{52.14}{168} = .3103$. The titration is effected in the manner directed for the determination of iron in iron ores.

Barba's Modifications.

Barba * has suggested several modifications which decidedly improve the method. To avoid the large precipitate of manganese dioxide, he uses nitric acid to oxidize the iron, having found that even a considerable excess of this reagent does not affect the subsequent reactions. He uses, most successfully, ammonia to destroy the excess of potassium permanganate. The method is as follows:

Dissolve 1.25 grammes steel in 20 c.c. sulphuric acid (1.2 sp. gr.). When solution is complete, add nitric acid drop by drop until the iron is oxidized; 5 c.c. of nitric acid (1.2 sp. gr.) is generally sufficient.

Boil to remove nitrous fumes, and add hot water to bring the volume to 150 c.c.; add from a pipette 5 c.c. of a saturated solution of potassium permanganate and boil briskly for from fifteen to twenty minutes; remove from the plate, wash down the sides of the beaker to remove all permanganate, and add 25 c.c. strong ammonia down the side of the beaker; shake well, and replace on the cooler part of the plate to avoid

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* The Iron Age, lii. 153.

"bumping," of which there is some danger if the heat be raised too rapidly. Shake occasionally and digest for about fifteen minutes, or until the permanganate is all decomposed, then add cautiously 20 c.c. dilute sulphuric acid (1.58 sp. gr.) and bring gently to boiling. Cool the solution and pour into a graduated 250 c.c. flask. Make up to mark with cold water, and mix well by pouring back and forth into a dry beaker a few times. Allow the precipitate to settle, and filter through superposed funnels, with close, hard, dry filters, into a dry beaker; measure off 200 c.c. (equal to 1 gramme sample) of the clear filtrate, titrate by adding a known excess of ferrous sulphate, and determine the excess by standard permanganate.

DETERMINATION OF ALUMINUM.

Stead's Method.*

Weigh 6, 12, or 24 grammes steel, place in a 600 c.c. beaker, cover with a watch-glass, dissolve in hydrochloric acid (strong), evaporate to dryness, redissolve in hydrochloric acid, filter into a 1000 c.c. beaker through an ashless filter, nearly neutralize the filtrate with dilute ammonia, and boil. The filtrate should measure 500 or 600 c.c. Add to the solution 1 or 2 c.c. of saturated solution of ammonium phosphate, and then a large excess of sodium hyposulphite, boil till all sulphurous acid has passed off (half an hour's boiling should be sufficient); just before filtering add 20 c.c. of a saturated solution of ammonium acetate, stir to mix, and filter through an ashless filter, wash precipitate and filter five or six times, add to the beaker in which the precipitate had been formed 10 c.c. hydrochloric acid, heat to boiling, remove the vessel containing the filtrate, and instead of it place under the funnel a platinum dish, and pour over the filter the boiling acid. Rinse out the beaker and wash all soluble matter on the filter with a fine jet, evaporate the solution to dryness in the platinum dish, and heat to a temperature of 300° or 400° F. on the hot plate to drive off excess of acid.

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* Prepared by Mr. J. E. Stead, of Middlesboro', England, for this volume.

Add from 2 to 5 grammes pure sodium hydrate made from sodium free from aluminum and about 2 c.c. water. Heat gently over a rose-burner for ten minutes, maintaining the mass in a fluid state all the time. Cool and add water, and boil till solution is complete. Make the bulk of the solution to 300 c.c. and note the temperature exactly. Shake well and filter through an ashless filter. Measure off 250 c.c. at the original temperature, equal to 5, 10, or 20 grammes steel. If any yellow tint is observable chromium may be present. In this case the aluminum phosphate must be neutralized with hydrochloric acid and precipitated by ammonium carbonate, taking care to boil the solution well to free from excess of ammonia before filtering. Filter through an ashless filter, dry, burn, and weigh, dissolve the precipitate in hydrochloric acid and determine phosphoric acid in it, and deduct the weight found from the weight of the original precipitate. If chromium is absent, neutralize the solution with hydrochloric acid as before described, boil and add excess of sodium hyposulphite, and boil for half an hour, filter off the precipitate, burn, and weigh as pure aluminum phosphate, which contains 22.18 per cent. of aluminum.

Carnot's Method.*

M. Carnot states that the method is very similar to that published by Mr. J. E. Stead in the *Journal of the Society of Chemical Industry*, 1889, page 965, but that he had used and taught it in the École des Mines for eight years. It is founded on the reaction that he pointed out in 1881, that aluminum is precipitated as the neutral phosphate from a boiling solution faintly acid with acetic acid. The precipitation succeeds equally well when the solution contains iron, if the ferric salt has been previously reduced to ferrous by sodium hyposulphite.

Treat 10 grammes of the iron or steel in a platinum dish covered with a piece of platinum-foil with hydrochloric acid, and when solution is complete, dilute and filter into a flask, washing the carbon, silica, etc., on the filter thoroughly with distilled water. Neutralize the solution with ammonia and sodium carbonate, but see that no permanent precipitate is formed, then add a little sodium hyposulphite, and, when the liquid—at first violet—becomes colorless, 2 or 3 c.c. of a saturated solution of sodium phosphate and 5 or 6 grammes of sodium acetate dissolved in a little water. Boil the solution about three-quarters of an hour, or until it no longer smells of sulphurous acid. Filter, and wash the precipitate of aluminum phosphate, mixed with a little silica and ferric phosphate, with boiling water. Treat the precipitate on the filter with hot dilute hydrochloric acid, allow the solution to run into a platinum dish, evaporate to dryness, and heat at 100° C. for an hour to render the silica insoluble. Dissolve in hot dilute hydrochloric acid, filter from the silica, dilute to about 100 c.c. with cold water, neutralize as before, add a little hyposulphite in the cold, then a mixture of 2 grammes of sodium hyposulphite and 2 grammes of sodium acetate, boil for one-half hour, wash, and weigh as aluminum phosphate, which contains 22.18 per cent. of aluminum.

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* A. Carnot, Moniteur Scientifique, 1891, p. 14.

Ether Method.

Treat 5 grammes of steel as described for the determination of nickel and evaporate the hydrochloric acid solution, which may contain nickel, chromium, copper, etc., until the ether is driven off, add a few drops of nitric acid or bromine to oxidize the iron, and precipitate by ammonia. Boil for a few minutes, filter, and wash; redissolve in hydrochloric acid, and reprecipitate, filter, and wash with boiling water. The precipitate will contain only iron, aluminum, and chromium. When chromium is absent, dissolve the precipitate in hydrochloric acid, evaporate to dryness, dissolve in a few drops of hydrochloric acid, filter, and dilute with cold water to 100 c.c., add 2 or 3 c.c. of sodium phosphate, and proceed as in the second precipitation of aluminum phosphate by Carnot's method.

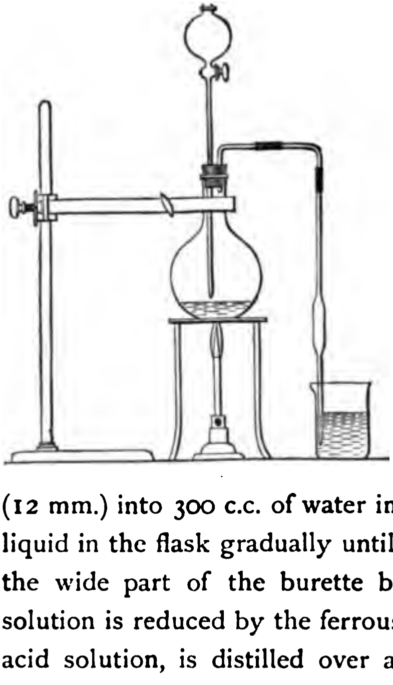
When chromium is present, fuse the precipitate of ferric oxide, alumina, and chromic oxide with sodium carbonate and a little sodium nitrate, dissolve in water, add ammonium nitrate, boil well, and filter. The chromic acid will be in the filtrate and the ferric oxide and alumina will be insoluble. Dissolve in hydrochloric acid and proceed as when chromium is absent.

DETERMINATION OF ARSENIC.

By Distillation.

Lundin * has suggested the following method of determining arsenic, which gives very good results. Dissolve 10 grammes of drillings in a large beaker in nitric acid (1.2 sp. gr.), transfer the solution to a platinum or porcelain dish, add 50 c.c. sulphuric acid, and evaporate until copious fumes of sulphuric acid are given off. Cool the dish, add 50 c.c. of water, and evaporate again until the excess of sulphuric acid is driven off, and the ferric sulphate is so dry that it can readily be transferred to a flask of about 500 c.c. capacity. Add to the mass in the flask 15 grammes finely powdered ferrous sulphate, pour in 150 c.c. strong hydrochloric acid, and close the flask with a stopper carrying a tube bent twice at right angles and connected by a rubber tube with a 50 c.c. pipette, the point of which dips about ½ inch (12 mm.) into 300 c.c. of water in a beaker, as shown in Fig. 91. Heat the liquid in the flask gradually until it boils, and continue the distillation until the wide part of the burette becomes heated. The arsenic acid in the solution is reduced by the ferrous sulphate, and, in the strong hydrochloric acid solution, is distilled over as arsenious chloride. Remove the light, disconnect the pipette, heat the solution in the beaker to about 70° C., and pass a rapid current of hydrogen sulphide through it until it is completely saturated. Remove the excess of hydrogen sulphide by a current of carbonic acid, and when the solution smells very faintly of hydrogen sulphide, filter off the yellow precipitate of arsenious sulphide on a Gooch

FIG. 91.



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* Jern-Kontorets Annaler, 1883, p. 360; Chem. News, li. 115.

crucible or on a counterpoised filter,* wash with water, then with alcohol, then with pure carbon disulphide, dry at 100° C., and weigh as arsenious sulphide, which contains 60.93 per cent. of arsenic.

Or, after filtering the precipitate on the felt in a Gooch crucible, transfer the precipitate and felt to a small beaker, add a little fuming nitric acid, and, when action has nearly ceased, heat gently until the sulphur is dissolved, dilute, filter, and evaporate to about 10 c.c. Add 5 c.c. of magnesia-mixture and then ammonia equal to one-half the volume of the solution. Stir the solution vigorously from time to time, keeping it cool by immersing the beaker in ice-water, and allow it to stand twelve hours. Filter on a Gooch crucible, wash the precipitate of ammonium-magnesium arsenate with the ammonia-water containing ammonium nitrate, used for washing the ammonium-magnesium phosphate (page 85), dry at 103° C. for half an hour, then increase the heat very gradually to redness, and ignite strongly for a few minutes. Weigh as magnesium arsenate, which contains 48.30 per cent. of arsenic.

DETERMINATION OF TIN.

Tin is a most unusual constituent of steel or iron, but has been found in the former in cases where scrap from tinned iron, from which the tin has been removed by a chemical process, has been melted in the open-hearth furnace as a portion of the charge. Dissolve 10 grammes of the sample in hydrochloric acid, dilute to 600 c.c., and saturate the solution with hydrogen sulphide. Allow it to stand for several hours, filter, and wash with water containing hydrogen sulphide. Treat the precipitate on the filter with ammonium sulphydrate, allowing the solution and washings to run into a 250 c.c. beaker. Acidulate with acetic acid, allow to stand in a warm place for several hours, filter, and wash with water containing ammonium acetate made slightly acid with acetic acid. Dry the precipitate and filter, transfer the precipitate to a weighed porcelain crucible, burn the filter and add its ash to the precipitate, add a little sulphur, and ignite in a current of hydrogen sulphide, as directed for the determination of manganese as sulphide (page 112). Any arsenic present will be volatilized, but it is not possible to weigh the tin as sulphide, as its composition is not constant. Heat the crucible carefully, and roast the precipitate with access of air, heat it strongly two or three times with ammonium carbonate to volatilize any sulphuric acid that may have been formed, cool, and weigh as stannic oxide, which contains 78.81 per cent. of tin.

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* See page 28.

DETERMINATION OF TUNGSTEN.

Dissolve from 1 to 10 grammes of the drillings in nitric acid (1.2 sp. gr.), evaporate to dryness in the air-bath, redissolve in hydrochloric acid, dilute slightly, and boil for some time. The tungstic acid is deposited as a yellowish powder. Dilute, filter, wash with hot water containing a little hydrochloric acid, and finally with alcohol and water. The precipitate consists of tungstic acid mixed with more or less silica, graphite, and perhaps a little ferric oxide, titanic acid, etc. Dry and ignite the filter and precipitate, and burn off the carbon. Allow the crucible to cool, moisten the precipitate with water, add a little sulphuric acid and an excess of hydrofluoric acid. Evaporate to dryness under a hood, and ignite to drive off the sulphuric acid. Fuse the residue with five times its weight of sodium carbonate, allow it to cool, dissolve in water, filter from any insoluble matter, and wash with water containing a little sodium carbonate. The filtrate contains all the tungsten, as sodium tungstate. Nearly neutralize with nitric acid, and boil off the carbonic acid, allow the solution to cool slightly, and add a faint but distinct excess of nitric acid. Add an excess of mercurous nitrate,* and then mercuric oxide diffused in water,* until the free acid is all neutralized. The tungsten is all precipitated as mercurous tungstate, and can be washed perfectly free from sodium salts with hot water. Allow the precipitate to settle, filter on an ashless filter, wash with hot water, and dry the filter and precipitate. Separate the precipitate from the filter, burn the filter in a platinum crucible, add the precipitate, and heat it under a hood with a good draft, increasing the heat gradually to a bright red. The mercury volatilizes, and there remains only tungstic acid. Cool, and weigh as tungstic acid, which contains 79.31 per cent. of tungsten.

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* See page 56.

Rapid Method for Tungsten.

A rapid method for the determination of tungsten in high tungsten steels and one that gives results sufficiently accurate for ordinary work is as follows:

Treat 1 gramme of the steel in a No. 3 Griffin's beaker with 25 c.c. of aqua regia, evaporate to dryness, redissolve in 10 c.c. strong hydrochloric acid, add 1 or 2 c.c. strong nitric acid, heat for a few minutes, dilute with hot water to 100 c.c., and boil for ten minutes. Filter, wash with water containing a little hydrochloric acid, and ignite. Treat the precipitate in the crucible with a few drops of sulphuric acid and some hydrofluoric acid, evaporate to dryness, ignite, and weigh. Fuse the precipitate with a little sodium carbonate, dissolve in hot water, filter off the ferric oxide, wash it well with hot water, return it to the crucible, ignite, and weigh. The difference between the two weights is tungstic acid.

DETERMINATION OF VANADIUM.

Vanadium is occasionally found in pig-iron, and may be determined with great accuracy by the following method. Treat 5 grammes of the drillings with 50 c.c. nitric acid (1.2 sp. gr.) in a No. 4 beaker. When all action has ceased, transfer the liquid to a porcelain dish, evaporate to dryness, and heat at a gradually increasing temperature over a Bunsen burner until the nitrates are nearly all decomposed and the mass separates easily from the bottom and sides of the dish. Transfer the cooled mass to a porcelain or agate mortar, and grind it thoroughly with 30 grammes of dry sodium carbonate and 3 grammes of sodium nitrate. Transfer to a large platinum crucible, and fuse well for about an hour at a high temperature. Run the fused mass well up on the sides of the crucible, allow it to cool, dissolve in hot water, and filter. Dilute the filtrate to about 600 c.c., and add nitric acid carefully to get rid of the carbonic acid. Boil off the latter, but be careful to keep the solution always slightly alkaline. Filter, and to the filtrate add a few drops of nitric acid to make it faintly acid, when the appearance of a yellowish coloration is an indication of the presence of vanadic acid. Add to the solution a few c.c. of mercurous nitrate,* and then an excess of mercuric oxide in water,* to render the solution neutral † and insure the complete precipitation of all the mercurous vanadate. With the mercurous vanadate are precipitated also all the phosphoric, chromic, tungstic, and molybdic acids as mercurous salts. Heat to boiling, filter, and wash the precipitate. Dry it, separate the paper, burn it in a platinum crucible, add the precipitate, heat carefully to expel the mercury, and finally heat to full redness. Fuse the brownish-red mass remaining in the crucible with a little sodium carbonate and a pinch of sodium nitrate, dissolve the cooled mass in water, and filter into a small beaker. Add to the solution pure ammonium chloride in excess (about 3.5 grammes to each 10 c.c. of solution), and allow it to stand for some time, stirring occasionally. Ammonium vanadate, insoluble in a saturated solution of ammonium chloride, separates out as a white powder. It is necessary to keep the solution decidedly alkaline, and a drop or two of ammonia must be added from time to time. The appearance of the faintest yellowish tint to the solution is evidence that it has become slightly acid, and this must be corrected or the result will be too low. Filter on a small ashless filter, wash first with a saturated solution of ammonium chloride containing a drop or two of ammonia, and then with alcohol. Dry, ignite, moisten with a drop or two of nitric acid, ignite, and weigh as vanadic acid, which contains 56.22 per cent. of vanadium.

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* See page 56.

† Am. Chem. Jour., v. 373.

DETERMINATION OF MOLYBDENUM.

In irons and steels containing from 1 to 10 per cent. of molybdenum treat 1 gramme of the drillings in a beaker with from 50 c.c. to 100 c.c. nitric acid (1.2 sp. gr.), and heat on hot plate until all action has ceased, evaporate to dryness in an air-bath, take up with hydrochloric acid and heat until all ferric oxide is dissolved, evaporate to dryness, take up with dilute hydrochloric acid and filter from silica; treat this residue with sulphuric and hydrofluoric acids, weighing if silicon is to be determined, and after weighing the second time fuse the residue with sodium carbonate and a little sodium nitrate, dissolve in water, filter, and add filtrate to the main solution. Reduce the ferric chloride with ammonium bisulphite as in the determination of phosphorus (page 81 *et seq.*), and after having driven off the sulphurous acid, pass hydrogen sulphide gas into the solution for an hour, keeping it at about 80° C. At the end of this time make the solution ammoniacal, then acidulate with hydrochloric acid and pass hydrogen sulphide again for a few minutes; stand the beaker aside and allow the precipitate to settle until the supernatant liquid is clear, filter on paper, and wash with hydrogen sulphide water. Treat the filtrate again in the same way, and if any precipitate forms, filter on another paper. Wash the precipitates from the papers into a beaker with hot ammonium sulphide solution, burn the papers in a porcelain crucible, cover the residue in the crucible with flowers of sulphur and heat gently until the sulphur is melted, then add a little sodium carbonate, cover the crucible with a lid and heat until liquid; cool, dissolve in hot water, filter, and add the filtrate to the main solution. Warm the sulphide solution for an hour or so and filter, washing with ammonium sulphide water from any sulphides that may be insoluble in the ammonium sulphide, but which should be soluble in hydrochloric acid, unless some copper has dissolved in the previous treatment; otherwise the treatment with ammonium sulphide has been insufficient.

Heat the filtrate, which should be yellow in color, almost to boiling, and acidulate carefully with hydrochloric acid; when the acid is in excess, all the molybdenum sulphide will be precipitated, but hydrogen sulphide may be passed for a short time if necessary. Heat the solution gently until all smell of hydrogen sulphide is driven off, and filter on a weighed Gooch crucible, washing with hot water. Dry at 100° or 120° C. and ignite in a stream of hydrogen, until weight is constant, by placing the bowl of a clay tobacco-pipe in the crucible and passing the hydrogen into the stem. The hydrogen gas must have replaced the air in the pipe and crucible before the heat is applied. Heat to dull redness for one hour, remove the heat, and allow to cool with the hydrogen passing. Weigh, and repeat the ignition; the second weight will rarely differ much from the first. The precipitate is molybdenum disulphide, which contains 60 per cent. of molybdenum.

In Ferro-Molybdenum.

In ferro high in molybdenum .2 gramme is treated in a large platinum crucible with nitric acid (1.2 sp. gr.) until action has ceased; it is then run dry and gently ignited, fused with from 20 to 30 grammes sodium carbonate and 3 grammes sodium nitrate, dissolved in water, filtered, the residue again fused, dissolved, and filtered, the two filtrates added together, acidulated with hydrochloric acid, boiled to expel carbonic acid, and hydrogen sulphide passed to precipitate the molybdenum sulphide. From this point proceed as in iron and steel.

DETERMINATION OF NITROGEN.

This method is based on the reaction by which the nitrogen in iron or steel is converted into ammonia by hydrochloric acid during the solution of the steel in this reagent.

It was first published by A. H. Allen,* with many interesting details and results. The modifications of the method as described by Mr. Allen are by Prof. J. W. Langley,* of Pittsburg, and consist essentially in the use of caustic soda freed from nitrates and nitrites by the copper-zinc couple and subsequent distillation of all ammonia formed, and in a few details of manipulation.

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* Chem. News, xli. 231.

The reagents required are:

Hydrochloric Acid of 1.1 sp. gr., free from Ammonia, which may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel-tube and an evolution-tube, fill it half full of strong hydrochloric acid, connect the evolution-tube with a wash-bottle connected with a bottle containing the distilled water. Admit strong sulphuric acid free from nitrous acid to the flask through the funnel-tube, apply heat as required, and distil the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described farther on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1.1 sp. gr., and use the amount found as a correction.

Solution of Caustic Soda, made by dissolving 300 grammes of fused caustic soda in 500 c.c. of water, and digesting it for twenty-four hours at 50° C. on a copper-zinc couple, made, as described by Gladstone & Tribe, as follows. Place from 25 to 30 grammes of thin sheet zinc in a flask and cover with a moderately concentrated, slightly warm solution of copper sulphate. A thick spongy coating of copper will be deposited on the zinc. Pour off the solution in about ten minutes and wash thoroughly with cold distilled water.

Nessler Reagent. Dissolve 35 grammes of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition, until the red precipitate formed dissolves. Finally the precipitate formed will fail to dissolve, then stop the addition of the mercury salt and filter. Add to the filtrate 120 grammes of caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 litre. Add to this 5 c.c. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle, and decant or siphon off the clear liquid into a glass-stoppered bottle.

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* Communicated to the author.

Standard Ammonia Solution. Dissolve 0.0382 gramme of ammonium chloride in 1 litre of water. 1 c.c. of this solution will equal 0.01 milligramme of nitrogen.

Distilled Water free from Ammonia. If the ordinary distilled water contains ammonia, redistil it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 160 c.c. capacity are also required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1500 c.c. capacity, with a rubber stopper, carrying a separatory funnel-tube and an evolution-tube, the latter connected with a condensing-tube around which passes a constant stream of cold water. The inside tube, where it issues from the condenser, should be sufficiently high to dip into one of the glass cylinders placed on the working-table.

The determination of nitrogen is made as follows. Place 30 c.c. of the caustic soda, which has been treated with the copper-zinc couple, in the Erlenmeyer flask, add 500 c.c. of water, and distil until the distillate gives no reaction with the Nessler reagent. While this part of the operation is in progress, dissolve 3 grammes of the carefully washed drillings in 30 c.c. of the prepared hydrochloric acid, using heat if necessary. Transfer the solution to the bulb of the separatory funnel-tube, and when the soda solution is free from ammonia, drop the ferrous chloride solution into the boiling solution in the flask, very slowly. The ferrous hydrate formed is apt to stick to the bottom and sides of the flask and cause it to break. When about 50 c.c. of water have been collected in the cylinder, remove it and substitute another cylinder. Place 1½ c.c. of the Nessler reagent in a cylinder, dilute the distillate to 100 c.c. with the special distilled water and pour it into the cylinder containing the Nessler reagent. Take another cylinder, place 1½ c.c. of the Nessler reagent in it, and pour into it 100 c.c. of the special distilled water to which 1 c.c. of the ammonium chloride solution has been added, and compare the colors of the solutions in the two cylinders. If the solution in the cylinder containing the ammonium chloride solution is lighter in color than that in the cylinder containing the distillate, place 1 ½ c.c. of the Nessler reagent in another cylinder, pour into it 100 c.c. of water containing 2 or more c.c. of the ammonium chloride solution, and repeat this operation until the colors of the solutions in the two cylinders correspond after standing about ten minutes. When about 100 c.c. have distilled into the second cylinder, replace it and test as before. Continue the distillation until the water comes over free from ammonia, then add together the number of c.c. of ammonia solution used, divide the sum by 3, and each 0.01 milligramme will be 0.001 per cent. of nitrogen in the steel.

DETERMINATION OF IRON.

The combined carbon in steel and iron interferes with a direct determination of the amount of metallic iron by solution of the drillings in hydrochloric or sulphuric acid and direct titration. It is always necessary to oxidize the iron and carbonaceous matter in the solution, and the process may be carried out as follows:

Dissolve .5 gramme of the drillings in a small flask, as described for the determination of iron in iron ores, in hydrochloric acid, add potassium chlorate in small crystals until the iron is all oxidized and an excess of potassium chlorate is present, boil until all the yellow fumes have disappeared, and then proceed as in the determination of iron in iron ores (page 212). Instead of potassium chlorate, potassium permanganate or chromic acid may be used to oxidize the iron and destroy the carbonaceous matter. In pig-irons the most satisfactory method is to fuse .5 gramme of the borings in a large platinum crucible with 10 grammes sodium carbonate and 2 grammes potassium nitrate, dissolve in hot water, transfer to a small beaker, allow the ferric oxide to settle, decant on a small filter, and wash several times by decantation. After the last decantation, remove the beaker containing the filtrate and place the beaker containing the ferric oxide under the funnel. Dissolve any adhering oxide in the crucible with hydrochloric acid, dilute slightly, and pour it on the filter to dissolve the small amount of oxide, allowing the solution to run into the beaker. Wash the filter if necessary, add more hydrochloric acid to the solution in the beaker, evaporate down, transfer to a small flask, deoxidize, and titrate as before. In the case of puddled iron, it is necessary to subtract the iron in the "slag and oxides" from the total iron obtained as above to get the amount of *metallic iron* in the sample.

METHODS FOR THE ANALYSIS
OF
FERRO-CHROME, FERRO-SILICON, AND FERRO-TITANIUM.

DETERMINATION OF CARBON.

Carbon may be determined with a considerable degree of accuracy in some of these alloys by combustion with lead chromate and potassium chlorate in a glass tube, as described on page 129. The best method, however, is by fusion with potassium bisulphate (page 132).

DETERMINATION OF SULPHUR.

Fuse 2 grammes of the sample ground as fine as possible in an agate mortar with 15 grammes of sodium peroxide in a large nickel crucible. The heat should be applied very slowly and cautiously, as sodium peroxide gives up its oxygen at a low temperature and the amount of heat generated by the oxidation of the chromium, silicon, etc., of the alloys is very great. An alcohol blast-lamp should be used, as the sulphur in ordinary gas is liable to vitiate the result. As soon as the mass is liquid, raise the heat for a few minutes, run the fused mass well up on the sides of the crucible, and allow it to cool. Stand the crucible in a 400 c.c. beaker containing a little water, partly cover the beaker with a watch-glass, and throw a fine stream of cold water into the crucible from a wash-bottle. When the violent action has ceased, wash the fusion from the crucible and filter from the insoluble ferric oxide, etc., washing the insoluble matter with water containing a little sodium carbonate. Acidulate the filtrate with hydrochloric acid and evaporate to dryness, preferably in a porcelain beaker. When thoroughly dry, cool, add 20 c.c. of strong hydrochloric acid, and heat until in the case of ferro-chrome all the chromium is redissolved. Dilute with hot water, filter, wash thoroughly with hot water, neutralize with ammonia, add 20 or 30 drops of hydrochloric acid, heat to boiling, add 10 c.c. of a boiling saturated solution of barium chloride, and boil for half an hour. Allow the solution to stand in a warm place overnight, filter, wash thoroughly, ignite, and weigh the barium sulphate.

DETERMINATION OF SILICON.

Ferro-silicon which is capable of being decomposed by acids is treated like steel, except that from 1 to 2 grammes is sufficient for the determination of silicon. For those not decomposed by acids and for ferro-chrome and ferro-titanium proceed as follows. Fuse 1 gramme with 10 grammes of sodium peroxide, treat with water, and finally with hydrochloric acid. Evaporate to dryness in a platinum or porcelain dish. When platinum is used for the evaporation, it is best to add an excess of sulphurous acid to the solution to prevent action on the platinum by the chlorine liberated by the action of the hydrochloric acid on the chromic or manganic acid in the solution.

Redissolve in hydrochloric acid and water, filter, wash, ignite, and weigh. Treat the weighed silica, etc., in the crucible with hydrofluoric and sulphuric acids, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica, which contains 47.02 per cent. of silicon.

In ferro-titanium, when filtering off the silica, etc., the greater part of the titanic acid will be with the silica, and as it has a tendency to pass through the filter when washed with water, the washing must be done with dilute hydrochloric acid. Instead of treating the ignited residue with hydrofluoric and sulphuric acids, it is better to fuse it with potassium bisulphate, which dissolves the titanic acid; dissolve the fused mass in water, filter, ignite, and weigh the silica as above.

DETERMINATION OF PHOSPHORUS.

In Ferro-Chrome.

Fuse 2 grammes of the finely ground material with 15 grammes of sodium peroxide in a nickel crucible, and treat it with water as directed for the determination of sulphur. The aqueous solution will contain sodium chromate and phosphate, besides silica, etc. Filter, and wash with water containing a little sodium carbonate. Acidulate he filtrate with nitric acid, heat to drive off the carbonic acid, add a little ferric chloride solution, add ammonia until the solution is alkaline to litmus-paper, and then acidulate with acetic acid. Boil for a few minutes, filter, and wash the precipitate of ferric phosphate and hydrate with hot water. Dissolve the precipitate on the filter in hot dilute hydrochloric acid, evaporate the solution to dryness, redissolve n a few drops of hydrochloric acid, and, if there is an appreciable amount of silica, dilute and filter, evaporate to a small bulk, and drive off the hydrochloric acid with nitric acid. In the absence of any material amount of silica, omit the filtration, add nitric acid, and evaporate to get rid of the hydrochloric acid. Transfer the nitric acid solution to a flask, precipitate by molybdate solution, and determine the phosphorus as described on page 92 *et seq.*

In Ferro-Silicon.

Fuse 2 grammes with sodium peroxide as described above, treat with water, and filter. As the solution contains a large amount of silica, evaporate to dryness after acidulating with hydrochloric acid, redissolve in water and hydrochloric acid, and filter. To the filtrate add a little ferric chloride solution, and proceed as in the case of ferro-chrome.

In Ferro-Titanium.

Fuse 2 grammes as described above, treat with water, and filter. The titanic acid will be insoluble as sodium titanate. Acidulate the filtrate with hydrochloric acid, add ferric chloride solution, and proceed as in the case of ferro-silicon.

DETERMINATION OF MANGANESE.

Proceed as in the determination of silicon, and, after filtering off the silica, evaporate the filtrate nearly to dryness, add nitric acid and evaporate off the hydrochloric acid, precipitate by potassium chlorate, and determine the manganese as in Ford's method (page 113).

DETERMINATION OF CHROMIUM.

Gravimetric Method.

Fuse ½ gramme with 5 grammes of sodium peroxide in a nickel crucible, treat with water, and filter. If the residue insoluble in water does not dissolve completely in hydrochloric acid, filter, ignite, and fuse the residue in sodium peroxide. Dissolve in water, and if the solution is yellow, filter and add the filtrate to the first filtrate.

To the united filtrates add ammonium nitrate in sufficient quantity to convert all the sodium salts into nitrates, boil until the excess of ammonia is driven off, filter, and to the filtrate in a large platinum or porcelain dish add an excess of sulphurous acid. This will reduce all the chromic acid to chromium sesquioxide. Boil off the sulphurous acid, add an excess of ammonia, boil, filter, and wash thoroughly with boiling water. Dissolve the precipitate in hot hydrochloric acid, evaporate to dryness, redissolve in hydrochloric acid, filter, and reprecipitate with ammonia. Boil, filter, wash, and ignite. Transfer the precipitate to a small beaker with water, add a little ammonium nitrate and a few drops of sulphurous acid, and boil until the solution no longer nells of sulphurous acid. Add a little ammonia, boil, filter, wash ith water containing ammonium nitrate, ignite, and weigh as chromium squioxide, which contains 68.48 per cent. of chromium.

Volumetric Method.

Fuse ½ gramme as above, treat with water, filter, and wash. oil the filtrate thoroughly to decompose all the sodium peroxide, idulate with sulphuric acid, cool, add an excess of ferrous sulphate, d titrate with a standard solution of potassium bichromate. The romium is calculated as in the volumetric method for chromium steel (page 190).

The use of permanganate is inadmissible, as the intense green lor of the solution masks the end reaction.

DETERMINATION OF IRON.

Fuse ½ gramme of the fine powder in a platinum crucible with grammes of sodium peroxide. Do not heat the fusion after it has ecome liquid, as the sodium peroxide cuts the platinum crucible. A ickel crucible cannot be used, as all nickel crucibles contain appreciable mounts of iron, so that the amount of iron derived from the nickel epends on the extent of the action on the crucible. Treat the fused mass ith water and filter. Dissolve the residue, which contains all the iron, hydrochloric acid, reduce with zinc, and titrate with permanganate in e usual way.

In ferro-titanium, as the titanic acid is with the iron, it cannot be educed with zinc, and reduction with ammonium sulphite, as in the case f titaniferous iron ores (page 215), must be resorted to.

METHODS FOR THE ANALYSIS

OF

IRON ORES.

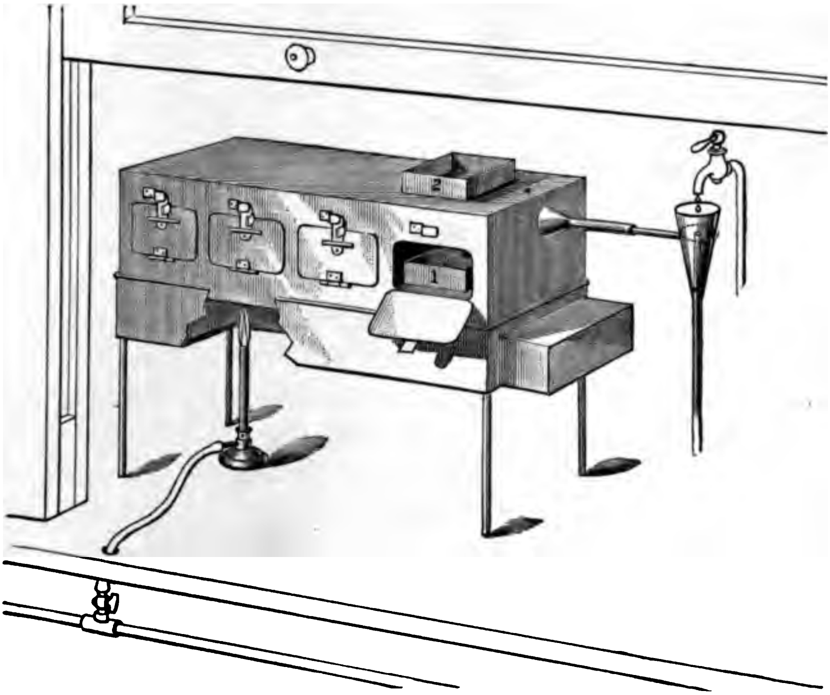
A FEW words in regard to the proper method of taking samples of iron ores may not be amiss, for unless the sample truly represents the lot from which it is taken, the subsequent work of the analyst is useless, if not misleading.

In drawing a sample, note carefully the relative amounts of fine ore and lumps in the lot to be sampled, and see that this proportion be observed in the whole amount taken. A small trowel may be used for taking the fine ore, and only about a teaspoonful should be picked up at one time. In taking pieces from the lumps, it will never do to merely chip the outside, but each lump as selected should be broken and chippings no larger than a cherry taken from both the inside and the outside. In sampling from cars or wagons these points should be observed in each car or wagon, for it is rarely the case that the ore even from one mine is so uniform as to render this precaution unnecessary. In some cases the lumps are covered with dirt or gangue, making the outside of the lump poorer in iron than the inside, and on the other hand the lumps are merely masses of dirt coated with ore. Then the fine stuff may be much richer than the lumps, or it may be merely dirt or gangue, while it almost always contains more hygroscopic water than the lumps. The sample should be taken in tin cans with close-fitting lids, and the amount should be proportioned to the size of the lot sampled. Two pounds to ten tons is a good rule for large lots.

DETERMINATION OF HYGROSCOPIC WATER.

Break the sample down quickly to about pea size, mix thoroughly in a large glazed earthenware or metal dish, and weigh out from ½ to 1 kilo. into a copper box about 4½ inches (114 mm.) long, 3¾ inches (95 mm.) wide, and 1½ inches (38 mm.) deep, and dry in a water- or air-bath at 100° C. for at least twelve hours, or until it ceases to lose weight. Fig. 92 shows a convenient form of water-bath. The boxes are numbered, and each one is provided with a counterpoise stamped with the same number as the box, to facilitate the weighing. When a supply of water is not available to run the constant level shown in Fig. 92, the device, on the principle of Mariotte's flask, as shown in Fig. 83, page 172, may be used. The position of the end *b* of the tube *a* fixes the level of the water in the bath.

FIG. 92.



A balance sensitive to .1 gramme is sufficiently accurate for weighing these samples. The loss of weight in grammes divided by 5, when ½ kilo. of ore was originally used, gives the percentage of hygroscopic water in the sample. Grind the dried sample very fine, mix it well, heat as much of it as may be required for the analysis in the water-bath, and put it while still hot into a perfectly dry, glass-stoppered bottle.

DETERMINATION OF TOTAL IRON.

Very few iron ores are completely decomposed by hydrochloric acid, the insoluble residue usually containing more or less iron, as silicate, titaniferous iron, etc. The disregard of this fact may occasion grave errors in the determination of iron, and, unless a previous examination has shown the absence of iron in the insoluble residue, it is best to proceed as follows. Place 1 gramme of the finely ground sample in a No. 1 beaker, add 10 c.c. hydrochloric acid, and digest it on the hot plate until the residue appears quite white and flotant, or until the acid appears to have no further action. When the ore contains carbonaceous matter, add a little potassium chlorate. Wash off the watch-glass with a fine jet of water, remove it, and evaporate to dryness in the air-bath. Redissolve in about 5 c.c. hydrochloric acid, dilute with 10 c.c. water, allow to settle, and decant the clear liquid into a flask of from 50 to 75 c.c. capacity. Transfer the residue to a small filter, fitted in a funnel placed in the neck of the flask, with as little water as possible, and wash with cold water from a fine jet. Transfer the filter to a small platinum crucible, burn it off, allow the crucible to cool, and pour on the residue 20 or 30 drops of sulphuric acid and about twice as much hydrofluoric acid. Heat carefully, and, if the residue is dissolved, evaporate off the hydrofluoric acid, allow the liquid to cool, and dilute slightly, when it will be ready to add to the solution in the flask, which will have been deoxidized in the mean time by one of the methods explained farther on.

Occasionally this treatment fails to decompose the insoluble residue, in which case heat the crucible until the greater part of the sulphuric acid is driven off; then add about .5 gramme potassium bisulphate, and heat gradually until the potassium bisulphate is quite liquid and fumes of sulphuric acid are given off whenever the lid of the crucible is raised. When all the black specks have disappeared, allow the crucible to cool, and dissolve the salt in the crucible with hot water and a few drops of hydrochloric acid.

Several methods are used for the deoxidation of the solution of ferric chloride, but the one in general use is by adding metallic zinc to the solution. The iron is deoxidized according to the reaction $Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2$, while the excess of hydrochloric acid is decomposed and hydrogen liberated, $2HCl + Zn = ZnCl_2 + 2H$. As all zinc contains a small amount of iron, the amount added to the solution should be roughly weighed. Add then to the solution in the flask 3 grammes of granulated zinc,* and, when the evolution of hydrogen has somewhat slackened, heat the flask slightly. The neck of the flask is closed by a small funnel, which allows the hydrogen to escape while the liquid is caught on the funnel and falls back into the flask. It sometimes happens as the solution becomes neutralized that a basic salt of ferric oxide is thrown down, giving the solution a reddish color; in this case add a few drops of hydrochloric acid, and when the solution finally becomes colorless add a few drops more of hydrochloric acid. If this fails to produce a yellowish coloration, the solution may be considered deoxidized. Pour in through the funnel the solution of the residue insoluble in hydrochloric acid, and add gradually a mixture of 10 c.c. sulphuric acid and 20 c.c. water. This addition of sulphuric acid is a very necessary part of the operation, for it not only serves to dissolve the remainder of the zinc which is unacted on when the deoxidation is complete, but it supplies the proper amount of zinc sulphate, which makes the end reaction with potassium permanganate as sharp as if no hydrochloric acid were present in the solution. As soon as all the zinc is dissolved, wash down the funnel inside and out and the neck of the flask with a fine jet of water, filling the flask almost full, cool the flask in water, and when the solution is quite cold transfer it to a large white dish of about 1500 c.c. capacity. Wash the flask and funnel well with cold water, pour the rinsing into the dish, and make the solution up to about 1000 c.c. Run in from a burette a standard solution of potassium permanganate (Marguerite's method), the value of which has been carefully determined by one of the methods described farther on. At first the color of the permanganate is destroyed almost as soon as it touches the liquid in the dish, which should be stirred carefully with a glass rod. The permanganate should be added more and more slowly until towards the end of the operation it is added only drop by drop. The liquid in the dish gradually assumes a yellowish tint, which is deeper the larger the amount of iron in the ore. Finally a drop of the permanganate seems to destroy the yellow color, and the next drop gives the liquid a very faint pink tinge. This is the end of the reaction. Take the reading of the burette, and then add another drop, which will cause the solution to become decidedly pink in color. The number of c.c. of the standard solution used when the reading was taken, less a small correction for the zinc, etc., noted farther on, multiplied by the value of 1 c.c., gives the amount of metallic iron in the ore.

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* See page 58.

The simple form of reductor (Fig. 52) shown on page 94 may be used for deoxidizing the solution of the ore in which the iron is in the form of sulphate. With amalgamated zinc it is a most excellent and rapid device. The method of reduction is given on page 95 in the description of the method of standardizing the potassium permanganate solution.

When using a standard solution of potassium bichromate (Penny's method), the end reaction is not rendered apparent by a change in the color of the solution, but the presence or absence of ferrous salt in the solution is determined by taking a drop from the dish on the end of the stirring-rod and allowing it to run into a drop of a dilute, freshly made solution of potassium ferricyanide placed on a white tile or capsule. Dissolve a very small crystal of potassium ferricyanide in a few c.c. of water, and place a number of drops of the solution on a white tile or on a flat-bottomed capsule. Run the carefully standardized solution of potassium bichromate from the burette into the deoxidized iron solution previously placed in a white dish. The solution, at first colorless, changes gradually to a decided chrome-green from the reduction of the chromic acid. Test the progress of the oxidation of the iron solution by transferring a drop of it on the end of the stirring-rod to one of the drops of ferricyanide. As the blue color produced becomes less intense, add the bichromate more slowly and make the test more frequently, towards the end of the operation after the addition of each drop of bichromate. When, finally, no color appears in the test-drops, even after the lapse of several moments, the oxidation of the ferrous salt is complete, and the amount of bichromate used, less a small correction for the zinc, is the measure of the amount of iron in the ore. The potassium ferricyanide employed must, of course, be perfectly free from ferrocyanide: it may be tested by adding a drop of ferric chloride solution to one of the drops of ferricyanide solution, the absence of any resulting blue color in the test-drops being proof of the purity of the ferricyanide. As towards the end of the operation the frequent tests become rather tedious, some analysts prefer to make the determinations in duplicate, using the first to get an approximate result.

When the ore is completely decomposed by hydrochloric acid, a separate treatment of the residue is unnecessary, and the ore may be weighed at once into the flask and treated with 10 c.c. hydrochloric acid and a little potassium chlorate when organic matter is present. When the ore is completely decomposed, and any chlorine from the potassium chlorate driven off, add 30 c.c. of water, and proceed with the deoxidation.

Instead of deoxidizing the solution of ferric chloride by zinc, it may be deoxidized by a solution of ammonium bisulphite. In fact, the deoxidation by zinc is not practicable in ores containing much titanic acid, for the titanic acid is reduced by metallic zinc to titanic oxide, imparting a purple or blue color to the solution, and acting like a solution of ferrous salt on the standard solution of permanganate. In deoxidizing a solution of ferric chloride by this method it should be placed in a flask of 120 c.c. capacity, and two or three small spirals of platinum wire added to facilitate the subsequent boiling. Add cautiously to the solution (which should not exceed 40 c.c. in volume) enough ammonia to produce a slight permanent precipitate of ferric hydrate, which remains even after vigorous shaking. Add now 5 c.c. of a strong solution of ammonium bisulphite,* shake vigorously, and warm the flask gently. As the color of the solution (at first a deep red) fades, increase the heat, and finally heat to boiling. When the solution is colorless, add to it the solution of the residue and 100 c.c. sulphuric acid mixed with 20 c.c. water. Boil the solution until all the sulphurous acid is driven off. When the escaping steam no longer smells of sulphurous anhydride, place the flask in cold water, wash down the funnel and the neck of the flask, filling the latter full of water, and when the solution is cold transfer it to a dish and titrate with a standard solution.

A third method of deoxidizing the solution of ferric chloride is used, in which the reducing agent is a solution of stannous chloride. The investigations of Zimmerman † and Reinhardt ‡ have made this method of reduction a favorite one, especially when, by the use of phosphoric acid and manganous sulphate, the subsequent titration with potassium permanganate is practicable. The details are as follows. Prepare the following solutions:

1. Phosphoric acid solution. Dissolve 200 grammes of crystallized manganous sulphate in 1 litre of water, add a few drops of sulphuric acid, and filter. Add to this 1 litre of phosphoric acid (1.3 sp. gr.), 600 c.c. water, and 400 c.c. strong sulphuric acid.

2. Stannous chloride solution. Dissolve 120 grammes of granulated tin, free from iron, in 500 c.c. hydrochloric acid (1.19 sp. gr.), dilute to 1 litre, and filter through asbestos. To the filtrate add 1 litre of hydrochloric acid (1.124 sp. gr.) and 2 litres of water.

3. Mercuric chloride solution. Dissolve 50 grammes of mercuric chloride in 1 litre of water and filter.

Dissolve 1 gramme of the ore in 30 c.c. strong hydrochloric acid (if necessary, ignite, and fuse the residue with a little sodium carbonate, dissolve in water and hydrochloric acid, and add to the main solution), transfer to a 150 c.c. Erlemeyer flask, heat to boiling, and add, from a burette, stannous chloride solution until the color of the solution fades completely. Pour into the dish 600 c.c. of water and add to it 60 c.c. of the phosphoric acid solution. To the deoxidized solution in the flask add 60 c.c. of the mercuric chloride solution, pouring it all in at once, shake vigorously and wash the solution out into the dish, using plenty of wash-water, and titrate with permanganate in the usual way. The phosphoric acid makes the solution nearly colorless by forming ferric phosphate, and the end reaction is very sharp.

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* See page 44.

† Berichte d. Chem. Ges., 1884, xv. 779.

‡ Chem. Zeit., xiii. 324.

The mercuric chloride should not be added until everything is ready for the titration, as the absence of any deoxidizing substance may cause the solution to become slightly oxidized on standing.

Mixer and Dubois * give several modifications of the method as used in the Lake Superior region. They employ a solution of potassium permanganate of such strength that 1 c.c. equals 2 per cent. of iron when .5 gramme of ore is used. They use for standardizing the permanganate an iron ore the amount of iron in which is accurately known, and if the permanganate is not exactly of the proper strength, such a weight of the ore is taken, approximating .5 gramme, that the reading of the burette multiplied by 2 gives the percentage of iron. Necessarily this implies the use of the same weight of the ore to be analyzed. They also add to the ore about 2.5 c.c. of a 25 per cent. solution of stannous chloride before adding the hydrochloric acid, as this is said to very much hasten the solution of the ore.

Methods for Standardizing the Solutions.

It is of the utmost importance that the value of the standard solution employed should be determined with the greatest accuracy if the results obtained by its use are to be anything but mere approximations. To do this, not only should the reagents employed be pure, but the conditions under which the standard is fixed should be, as nearly as practicable, those under which it is employed in actual use. The conditions referred to are not only those of temperature, dilution, etc., but of the actual chemical composition of the liquid acted on by the standard solution by which its value is determined.

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* Journal of the American Chem. Soc., xvii. 405.

The best reagent to employ is a solution of ferric chloride of known strength. To prepare this, dissolve 100 grammes of wrought iron (free from manganese and arsenic, and in which the phosphorus has been accurately determined) in nitric acid, evaporate to dryness in a capsule, and heat until the iron nitrate is largely decomposed and the mass separates easily from the bottom and sides of the capsule. Transfer to a piece of platinum-foil with the edges turned up, and heat for some time in a muffle at a very high temperature, or heat it, a portion at a time, in a crucible at the highest temperature obtainable by a blast-lamp. Grind the entire mass very fine in an agate mortar, dissolve in hydrochloric acid, evaporate to dryness, redissolve in dilute hydrochloric acid, filter to get rid of silica, and dilute the solution to about 4 litres. 20 c.c. of this solution will contain about .5 gramme iron, and it may be kept indefinitely in a glass-stoppered bottle sealed with paraffine, or after being thoroughly mixed it may be preserved in a number of smaller bottles properly secured.

Wash out and dry thoroughly three of the small flasks used for deoxidizing the solutions of the ores, weigh them to within 1 mg., and measure into each a portion of the ferric chloride solution ranging from 15 to 25 c.c. in volume. Weigh the flasks and their contents; the differences between the first and second weights are the weights of the ferric chloride solution taken. Transfer the solution carefully from each flask to a platinum dish, dilute, boil, precipitate by ammonia, filter, wash, dry, ignite, and weigh the precipitate with the precautions mentioned farther on. The precipitate is ferric oxide + phosphoric acid. Subtract from this weight the amount of phosphoric acid in this weight of the material, and the remainder will be the weight of ferric oxide in the amount of solution used. Suppose, for example, that the original iron contained .1 per cent. phosphorus, this would be equivalent to 0.229 per cent. phosphoric acid, but, as the iron has been oxidized to ferric oxide, the percentage of phosphoric acid in the iron as oxide would be only $\frac{7}{10}$ as great as in the iron itself, the weight as oxide being $\frac{10}{7}$ as great as it was as iron. Therefore multiply .229 per cent. by .7 for the percentage of phosphoric acid in the ferric oxide, which gives .16 per cent. phosphoric acid. If we further suppose that the weight of ferric oxide + phosphoric acid obtained was .8131 gramme, .16 per cent. of this would be .0013 gramme, the weight of phosphoric acid in the precipitate, and .8131 — .0013 = .8118 gramme, the weight of ferric oxide in the amount of solution taken. Divide this weight by the weight of the solution, and the result is the weight of ferric oxide in 1 gramme of the solution of ferric chloride. Take the mean of the three results obtained in this way, and call this result the value of the ferric chloride solution in ferric oxide, or multiply by .7 for its value in iron.

To standardize the permanganate or bichromate solution, weigh out three portions of the ferric chloride solution into the flasks, reduce them by the method selected, and titrate the reduced solutions exactly as directed above. Before calculating the strength of the standard solution a small correction must be applied to the burette reading, due to the fact that a definite amount of oxidizing solution is required to produce the end reaction in all cases where permanganate is used, and, when bichromate is used, in those cases where zinc has been the deoxidizing agent.

Treat 3 grammes of zinc in a small flask with 5 c.c. hydrochloric acid and 20 c.c. water, add gradually 10 c.c. sulphuric acid and 20 c.c. water. When the zinc has all dissolved, place the flask in cold water until the solution is cold. Wash it out into the dish, dilute to 1 litre, add 20 c.c. ferric chloride solution (free from ferrous salt), and drop in the standard solution until the end reaction is obtained. Subtract the correction thus obtained from every burette reading. To calculate the strength of the standard solution, therefore, subtract the correction from the burette reading, and the result is the absolute volume of the standard solution required to oxidize the ferrous salt in the solution operated on. Knowing then the weight of the ferric chloride solution used, the amount of iron in each gramme of the solution, and the volume of the standard required to oxidize this amount, the value of each c.c. of the standard solution is found by multiplying the weight of ferric chloride solution used by the value of each gramme in iron, and dividing the amount by the number of c.c. of the standard used in titrating. The mean of the results obtained in the three portions used should be taken as the value of the standard solution. An example will illustrate the method of computation, and, as logarithms very much facilitate these calculations, they will be given in the example as well.

Weight of empty flask	22.8817	
Weight of flask + ferric chloride solution	40.0640	
Weight of ferric chloride solution used	17.1823	= log. 1.2350813
Value of ferric chloride solution, determined as on p. 218	1 gramme = .03227 gramme iron	= log. 8.5087990 − 10
Iron in ferric chloride solution used	.55448 gramme	= log. 9.7438803 − 10
Burette reading after titration	= 82.0 c.c.	
Less correction	0.25	
Corrected reading	81.75 c.c.	= log. 1.9124878
1 c.c. standard solution — .0067826 gramme iron		= log. 7.8313925 − 10

Of course in calculating the amount of iron in an ore it is only necessary to get the logarithm of the corrected reading (page 219) and add it to the logarithm of the standard solution as found above, the number corresponding to the resulting logarithm being the weight of iron in grammes in the ore. This multiplied by 100 will give the percentage.

Very fine iron wire may be used to standardize the solutions instead of a standard solution of ferric chloride. Weigh into the reducing flasks from .4 to .6 gramme of fine iron wire (page 55) which has been carefully rubbed with fine sand-paper and wiped clean with a linen rag. Dissolve in 10 c.c. hydrochloric acid and 20 c.c. water, with the addition of a few small crystals of potassium chlorate. Deoxidize carefully, and titrate as before directed. Multiply the weight of iron wire by .998 to get the absolute amount of iron used, apply the proper correction to the burette reading, and calculate the value of the standard.

Ferrous sulphate, $FeSO_4,7H_2O$,* containing 20.1439 per cent. iron, or the ferrous-ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$,† containing 14.2857 per cent., or almost exactly one-seventh of its weight of iron, may be used instead of ferric chloride solution or iron wire to determine the value of the standard solutions. The pure salts are generally weighed off, dissolved in water with 10 c.c. sulphuric acid added, and titrated direct, but they are not so satisfactory in use as the first and second methods described. It is important to have the standard solutions of the proper strength,—that is, neither too dilute nor too concentrated for convenience in working. As iron ores rarely contain more than 60 per cent. metallic iron, a standard solution 100 c.c. of which are equal to .66 gramme iron will be found sufficiently concentrated to avoid the necessity of refilling the burette for a determination; and where ores much poorer than this are habitually used the solutions may be correspondingly more dilute.

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* See page 56.

† See page 56.

When potassium permanganate is added to a solution of ferrous sulphate the reaction is $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$, or 316.2 parts by weight of potassium permanganate will oxidize 560 parts by weight of iron, or 3.727 grammes potassium permanganate to the litre will give a solution of about the strength required.

In the case of potassium bichromate the reaction is $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$, or 294.5 parts by weight of potassium bichromate will oxidize 336 parts of iron, or 5.785 grammes of potassium bichromate dissolved in 1 litre of water will give a solution 100 c.c. of which will be equivalent to about .66 gramme iron.

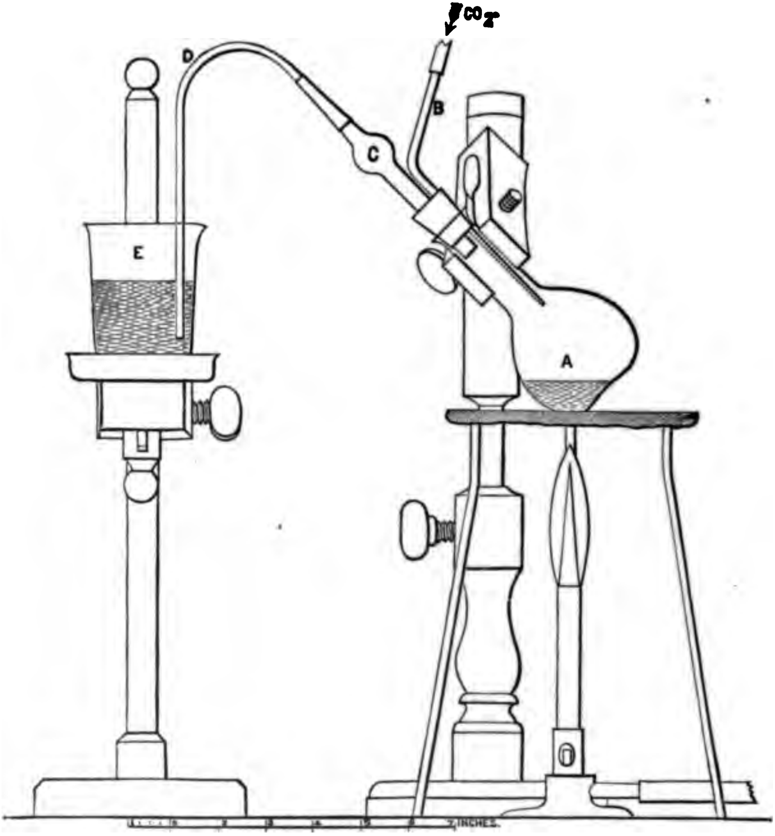
To prepare the solutions, therefore, dissolve the above weights, or multiples of them, in pure distilled water, allow the solution to stand for some little time, filter through asbestos, and dilute to the proper volume. Mix thoroughly by shaking in the bottle, and standardize as above directed. The solutions should be kept in glass-stoppered bottles in a dark closet, and the bottles should be well shaken whenever the solution is used.

DETERMINATION OF IRON EXISTING AS FERROUS OXIDE.

Many iron ores contain iron in the state of ferrous oxide, and this may be either soluble or insoluble in hydrochloric acid. To determine the ferrous oxide soluble in hydrochloric acid, weigh 1 gramme of the finely ground ore into the flask A, Fig. 93, of about 100 c.c.

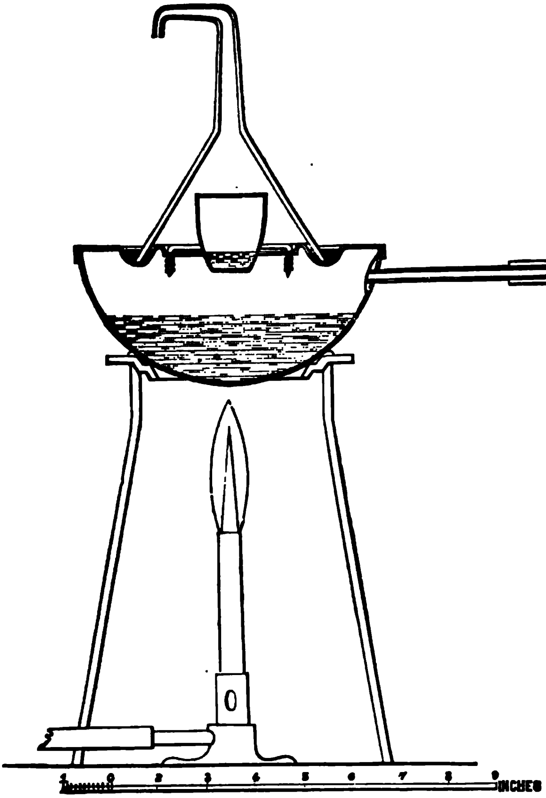
capacity. Close the flask with a rubber stopper fitted with the two glass tubes B and C, and place it in the position shown in the sketch. Connect the tube C by means of a piece of rubber tubing with the bent tube D dipping below the surface of the water in the beaker E. Pass a current of carbonic acid through the tube B until all the air is expelled, then remove for a moment the rubber tube connecting B with the source of carbonic acid, and by means of a small funnel and rubber tube introduce into the flask A, through B, from 10 to 12 c.c. strong hydrochloric acid, and establish the current of carbonic acid as before. Heat the flask carefully, and when the ore is entirely decomposed, or the

FIG. 93.



hydrochloric acid ceases to exert any further action on it, remove the source of heat, stop the current of carbonic acid for a moment, cool the flask with the hand, and allow the partial vacuum thus formed to draw the water from E back into A. Turn on the current of carbonic acid again, place a dish of cold water under the flask A, and allow the solution

FIG. 94.



to cool. Dissolve in a small flask 3 grammes of metallic zinc in 10 or 15 c.c. sulphuric acid, diluted with the proper quantity of water, cool it, and have it ready to pour into the titrating-dish by the time the solution in the flask A is cool. Wash the solution of the ore from the flask A into the dish, add the zinc solution, dilute to 1 litre, and titrate with a standard solution. Subtract from the burette reading the proper correction, calculate the percentage of iron, divide by 7, and multiply by 9. The result is the percentage of ferrous oxide in the ore soluble in hydrochloric acid. Allow the solution in the dish to stand for a few minutes, when all the undecomposed particles of ore will settle. Draw off the greater part of the clear supernatant fluid with a siphon, wash the sediment into a beaker with a jet of cold water, filter on a thin felt* in a Gooch crucible, and wash the sediment on the felt with cold water. Transfer the felt and sediment to a platinum crucible, pour into the crucible from 5 to 10 c.c. of hydrochloric acid and about half the quantity of hydrofluoric acid, cover the crucible, and place it in the water-bath shown in Fig. 94. The crucible rests on a platinum triangle fixed over the hole in the centre of the top of the bath. Around this hole is a groove in which a funnel stands as shown in the cut, while the water in the groove forms a tight joint.† Pass a current of carbonic acid or coal-gas through the tube in the side of the bath, as figured in the cut, to exclude the air, and heat the bath until the residue and felt are completely dissolved. Wash the crucible out into the titrating-dish into which have been poured just previously 3 grammes of zinc dissolved in sulphuric acid and enough cold water to make the solution up to nearly 1 litre. Titrate, and calculate the amount of ferrous oxide as before.

Of course separate portions of the ore may be used to determine the ferrous oxide soluble and insoluble in hydrochloric acid, but it is more troublesome, and experience has shown that it is no more accurate, and in some cases less accurate, than the method just described.

The total ferrous oxide may also be determined in one operation by treating 1 gramme of the ore direct in the crucible with 20 c.c. hydrochloric acid and 20 c.c. hydrofluoric acid, but it is often difficult to get the ore perfectly dissolved even by prolonged heating in the bath, and the ore must be ground very fine in the agate mortar. It is necessary to remove the funnel from time to time, raise the lid of the crucible, and stir the contents with a platinum wire.

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* The asbestos of which the felt is made must be free from ferrous oxide.

† Avery, Chem. News, xix. 270; Wilbur and Whittlesay, Crook's Select Methods, p. 133.

When the ore is completely decomposed by hydrochloric acid, or when the portion undecomposed contains no ferrous oxide, the treatment of the residue is unnecessary.

When an ore contains much organic matter, an accurate determination of ferrous oxide is often impossible, as the solution of the ore in hydrochloric acid reduces some of the ferric salt.

DETERMINATION OF SULPHUR.

Sulphur exists in two conditions in iron ores, as sulphur in the form of sulphides and as sulphuric acid in the form of sulphates. To determine the total sulphur, weigh 1 gramme of the finely ground ore into a large platinum crucible, add to it 10 grammes of sodium carbonate and a little potassium nitrate (less than 1 gramme *). Mix thoroughly with a platinum wire, and heat carefully over a large alcohol lamp until the mass appears perfectly liquid and in a tranquil state of fusion. Run the fusion well up on the sides of the crucible, allow it to cool, and treat it in the crucible with boiling water. Pour the liquid into a tall, narrow beaker, treat the crucible again with boiling water, and repeat the operation until all the sodium salts are dissolved and nothing remains in the crucible except the unavoidable stains. Stir the liquid in the beaker well and allow the iron oxide to settle. If the solution is colored red or green, it is proof of the presence of manganese in the ore; add a few drops of alcohol, which will precipitate the manganese as oxide, leaving the solution colorless unless the ore contains chromium, in which case the solution will be yellowish. Decant the supernatant liquid on a small filter, allowing the filtrate to run into a No. 4 beaker, fill the small beaker nearly full of hot water, stir well, and allow to settle. Decant again on the filter, and repeat the operation once more. Acidulate the collected filtrates with hydrochloric acid (about 20 c.c. will be required), evaporate to dryness in the air-bath, redissolve in water with a few drops of hydrochloric acid, filter into a No. 3 beaker, heat the filtrate to boiling, and add 10 c.c. of a boiling solution of barium chloride.* Allow to stand for some hours, filter on a Gooch crucible or on a small ashless filter, ignite, and weigh as barium sulphate, which multiplied by .1376 gives the weight of sulphur. The insoluble portion from the aqueous solution of the fusion may be used to determine the total iron in the ore, and is very convenient for this purpose in ores difficult to dissolve. Pour into the crucible in which the fusion was made about 10 c.c. of hydrochloric acid, place the lid on the crucible, and warm slightly to dissolve the adhering oxides, dilute with an equal bulk of water, and pour it on the small filter through which the aqueous solution was decanted, allowing it to run into the beaker which contains the residue of iron oxide, etc. Wash out the crucible, pouring the washings on the filter, and wash the filter free from ferric chloride with a jet of cold water. Evaporate the solution in the beaker to dryness, redissolve in 10 c.c. hydrochloric acid, and transfer the solution of ferric chloride, the silica, etc., to one of the small flasks, deoxidize, and titrate as directed.

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* See pages 46 and 48. It is well to make a blank determination, using the same amounts of sodium carbonate, potassium nitrate, and hydrochloric acid, applying the amount of barium sulphate found as a correction.

The sulphur which exists as sulphuric acid in an iron ore is usually combined with either calcium or barium: as calcium sulphate or of any of the other alkaline earths except barium, of the alkalies, or of the metals, it is soluble in hydrochloric acid; as barium sulphate it is practically insoluble. We may, therefore, determine the soluble sulphates as follows. Boil 10 grammes of the ore with 30 c.c. hydrochloric acid and 60 c.c. water, filter from the mass of the undissolved ore, evaporate the filtrate to dryness, redissolve in hydrochloric acid and water (1 to 2), filter into a No. 2 beaker, nearly neutralize by ammonia, heat to boiling, and precipitate by barium chloride solution. Filter and wash the precipitate, ignite and weigh as barium sulphate, which contains 34.352 per cent. sulphuric anhydride.

To determine the sulphuric acid which exists as barium sulphate, treat 10 grammes of the ore with 50 c.c. hydrochloric acid until the ore appears to be decomposed. Evaporate to dryness, redissolve in dilute hydrochloric acid (1 to 3), dilute, filter, and wash the insoluble matter thoroughly. Ignite and fuse the insoluble matter with sodium carbonate, treat the fused mass with hot water, and filter. In the filtrate is the sulphuric acid as sodium sulphate, while the barium remains on the filter as barium carbonate. It is safer to calculate the barium sulphate from the amount of barium rather than from the amount of sulphuric acid, as the ore may contain sulphides (pyrites, etc.) which are not decomposed by hydrochloric acid, but are decomposed and partly oxidized by fusion with sodium carbonate. The other forms of barium besides the sulphate (silicate and carbonate) are readily decomposed by hydrochloric acid, and are not likely to be found with the barium in the insoluble residue. It is, of course, possible to suppose the coexistence of barium silicate or carbonate and of calcium sulphate in an ore, and the consequent formation of barium sulphate when the ore is decomposed by hydrochloric acid; but, as the soluble sulphuric acid is determined in one operation and the insoluble in another,* the total amount of sulphuric acid existing as such is determined and the object of the analysis attained. To determine the barium, then, treat the insoluble matter obtained by the filtration of the aqueous solution of the fusion by dilute hydrochloric acid, evaporate to dryness to render the silica insoluble, redissolve in water with a few drops of hydrochloric acid, filter into a No. 2 beaker, heat the filtrate to boiling, and add a few drops of sulphuric acid diluted with a little water. Allow the precipitate to settle, filter, wash, ignite, and weigh as barium sulphate, from which weight calculate the amount of sulphuric anhydride in the ore insoluble in hydrochloric acid. To find the amount of sulphur existing as sulphides, subtract from the total sulphur the amount of sulphur in the sulphuric anhydride found as sulphates.

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* See page 51.

DETERMINATION OF PHOSPHORIC ACID.

Treat 5 or 10 grammes of the finely ground ore in 30 or 60 c.c. hydrochloric acid. (With low phosphorus ores use 10 grammes; with others, 5 grammes.) When the ore is decomposed, evaporate to dryness, redissolve in 20 or 40 c.c. hydrochloric acid, dilute, filter, and proceed exactly as directed in the determination of phosphorus in iron and steel (page 80 *et seq.*). The weight of the magnesium pyrophosphate multiplied by .63788 gives the weight of the phosphoric acid. The weight of the ammonium phospho-molybdate multiplied by .03735 gives the weight of the phosphoric acid.

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* The insoluble matter from the treatment of 10 grammes of the ore with hydrochloric acid for the determination of soluble sulphates (page 226) may be used to determine the barium sulphate.

Titanic acid is very generally found associated with iron ores, and may be regarded as one of the usual constituents. As mentioned on page 85, its presence, if overlooked, may lead to serious errors in the determination of phosphoric acid. When an ore contains much titanic acid it may readily be recognized by the peculiar milky appearance of the solution when it is diluted preparatory to filtering off the insoluble matter, and by the strong tendency it shows to run through the filter as soon as the attempt is made to wash the insoluble matter with water. Smaller quantities of titanic acid may be recognized by the clouding of the solution when it is deoxidized by ammonium bisulphite, as noted on page 88. In the latter case, however, this clouding may be caused by the formation of barium sulphate when the ore contains the latter element in the form of carbonate or silicate. Under these circumstances silica in the solution may also cause a cloud which closely resembles that of titanic acid, while barium sulphate may readily be distinguished from either by its granular appearance and its tendency to settle to the bottom of the beaker.

The insoluble residue from the solution of the ore in hydrochloric acid should, therefore, be treated to recover any phosphoric acid which may have remained insoluble in combination with titanic acid.* An additional test for the presence of titanic acid, and one that rarely fails even with very small amounts, is to dissolve the insoluble matter from the aqueous solution of the fusion of the residue from the hydrofluoric acid and sulphuric acid treatment of the insoluble portion of the ore in dilute hydrochloric acid, allowing it to run into a test-tube and adding metallic zinc. When titanic acid is present the solution first becomes colorless, then pink or purple, and finally blue from the formation of titanic oxide. The simplest way is to proceed as directed on pages 87 and 88 when using the acetate method, or on page 92 when using the molybdate method. These methods are not practicable, however, when the ore contains a very large amount of titanic acid, and recourse must be had to the method described on page 85, involving the fusion of the acetate precipitate and the residue from the treatment of the insoluble matter with hydrofluoric and sulphuric acids, with sodium carbonate and a little sodium nitrate. At any rate, it is best to pursue this method whenever titanic acid is also to be determined, as the same portion can be used for the estimation of both titanic acid and phosphoric acid, and the aggregate labor involved is much lessened.

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* When hydrofluoric acid is not available, fuse the residue with sodium carbonate, treat the fused mass with hot water, filter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness to render the silica insoluble. Redissolve in water with a little hydrochloric acid, filter, add a little ferric chloride, and make a separate acetate precipitation in this portion, adding the solution to the solution of the main acetate precipitation.

DETERMINATION OF TITANIC ACID.

The determination of titanic acid has always presented many difficulties, and its separation from a large amount of ferric oxide and alumina has been far from satisfactory, besides being most tedious. The principal sources of error in the estimation of titanic acid in iron ores are the tendency of phosphoric acid to prevent the precipitation of titanic acid by boiling when its sulphuric acid solution contains phosphoric acid and ferrous sulphate, and the liability of alumina to separate out with the titanic acid when the latter is precipitated under the circumstances above mentioned. There is also a mechanical difficulty, caused by the adhesion of the precipitated titanic acid to the bottom and sides of the beaker, from which it can sometimes be removed only by boiling with a strong solution of caustic potash. The admirable series of experiments carried out by Dr. Gooch * on the separation of aluminum and titanium suggests a method which renders the determination of titanic acid in iron ores much less troublesome, while adding greatly to the accuracy of the results. In carrying out the details of the method, dissolve 5 or 10 grammes of the ore in hydrochloric acid, and proceed exactly as in the determination of phos-

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* Proceedings Am. Acad. Arts and Sciences, New Series, xii. 435.

phoric acid, by fusing the residue from the treatment of the insoluble matter by hydrofluoric and sulphuric acids and the acetate precipitate with sodium carbonate and a little sodium nitrate,* and then complete the operation exactly as described in the determination of titanium in pig-iron.†

The essential points in this method are: 1. Separation of the titanic acid from the mass of ferric oxide by ammonium acetate in the deoxidized solution. 2. Separation from all the phosphoric acid and the greater part of the alumina by fusion with sodium carbonate, by which means a sodium titanate insoluble in water is formed, and at the same time sodium phosphate and aluminate soluble in that menstruum. 3. Separation of the last traces of alumina from the ferric oxide, lime, etc., by precipitating the titanic acid in the thoroughly deoxidized solution in the presence of a large excess of acetic acid and some sulphurous acid, the sulphuric acid being all in the form of sodium sulphate. The addition of a large excess of sodium acetate, by which this latter condition is effected, converts all the sulphate into acetates, and precipitates the titanic acid almost instantaneously as a hydrate, which is flocculent, settles quickly, shows no tendency to run through the filter, and is washed with the greatest ease. It sometimes happens that a little ferrous oxide is precipitated with the titanic acid, and the latter, after ignition, appears discolored; in this case fuse with a little sodium carbonate, add sulphuric acid to the cold fused mass, dissolve, and repeat the precipitation with sodium acetate in the presence of sulphurous and acetic acids exactly as in the first instance.

A number of experiments covering all the points involved in this method show it to be extremely accurate and entirely trustworthy.

DETERMINATION OF MANGANESE.

When manganese alone is to be determined in an ore, any one of the methods described under the determination of manganese in iron and steel (page 108) may be used. The most convenient, however, is Ford's method with the modifications necessary in the analysis of pig-iron (page 115). The only change requisite is to evaporate the solution in hydrochloric acid to dryness to render silica insoluble before filtering off the insoluble matter.

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* See page 47.

† See page 179.

In the determination of manganese in high grade manganese ores it is best to use a one-tenth factor weight (0.3874 gramme) of the sample, dissolve in hydrochloric acid, evaporate to dryness, redissolve in dilute hydrochloric acid, and filter off the insoluble matter. Ignite the insoluble matter in a platinum crucible, fuse with a little sodium carbonate, dissolve in water, acidulate with hydrochloric acid, and evaporate to dryness. Redissolve in dilute hydrochloric acid and filter into the main solution. Or, treat the ignited insoluble matter with sulphuric and hydrofluoric acids, drive off the hydrofluoric and the excess of sulphuric, cool, add water and a little hydrochloric acid, and heat until the residue dissolves, then add the solution to the main solution of the ore.

Evaporate the main solution until it is syrupy, add an excess of strong nitric acid and evaporate off the hydrochloric acid. Precipitate by potassium chlorate in the usual way and filter through asbestos. Wash the precipitate thoroughly with cold water to get rid of the calcium nitrate, which, being practically insoluble in strong nitric acid, will remain with the precipitated manganese dioxide unless this precaution be observed. There is no danger of dissolving the manganese dioxide by this treatment.

Proceed with the determination as directed on page 113. Each milligramme of manganese pyrophosphate is a tenth of one per cent. of manganese in the ore.

In using the acetate method it is, of course, necessary that all the iron should be in the form of ferric chloride, and also that there should be no reducing agent in the solution. Even a very small amount of ferrous chloride will cause the formation of a "brick-dust" precipitate, which cannot be kept from passing the filter while some of the iron remains dissolved in the acetate solution. When, therefore, the ore contains ferrous oxide, it should be oxidized by nitric acid or potassium chlorate, and the excess of the oxidizing agent removed by evaporation with hydrochloric acid.

Volhard's Method applied to High Grade Manganese Ores.

Volhard's is the most satisfactory volumetric method for high grade manganese ores. Dissolve 1 gramme of the ore in a small beaker in hydrochloric acid, heat until the chlorine is all driven off, wash out into a platinum dish (Fig. 36), and add 5 c.c. strong sulphuric acid and a little hydrofluoric acid. Evaporate to dryness and heat until the sulphuric acid begins to volatilize. Cool, dissolve in water, transfer to a 300 c.c. flask, and proceed as directed on page 116, except that 100 c.c. of the filtered solution represents one-third if a gramme of the ore is used.

It is necessary to heat the solution in the flask after there appears to be a slight excess of permanganate. This will make the precipitate settle rapidly and generally show the necessity for adding more permanganate.

A large number of comparative analyses have shown that it is necessary to add one one-hundredth of the amount obtained to get the true percentage of manganese; in other words, the results obtained are always one one-hundredth too low.

For instance, if by calculation the ore contains 50 per cent. of manganese by this method, the true result is 50.5 per cent.

Pattinson's Method.*

Dissolve in hydrochloric acid such a quantity of the sample as shall contain not more than .25 gramme of manganese. In high manganese ores add enough ferric chloride to the solution to make the iron and manganese contents about equal. Add calcium carbonate to the solution until it is slightly red in color and acidulate by adding hydrochloric acid until the red color disappears. Add sufficient zinc chloride in solution to give .5 gramme metallic zinc. Heat to boiling, dilute with boiling water to 300 c.c., and add 60 c.c. of a solution of calcium hypochlorite containing 33 grammes to the litre. To the solution of hypochlorite, just before using, add enough hydrochloric acid to give it a faint greenish tinge after agitation.

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* Society of Chemical Industry, vol. x. No. 4.

Finally add 3 grammes of calcium carbonate diffused in 15 c.c. of oiling water, and, after stirring well, 2 c.c. of methyl alcohol.

Filter on a large filter and wash with water at 65° C. until a strip f iodized starch paper gives no indication of chlorine.

Measure into a beaker 100 c.c. of a carefully standardized strongly acid olution of ferrous sulphate, containing 10 grammes of iron to the litre, nd place the precipitate and filter in it. When the precipitate has issolved add cold water and determine the excess of ferrous sulphate y a standard solution of potassium bichromate.

When the ore contains much organic matter it should be filtered off efore attempting to oxidize the ferrous salt, as it is quite impossible in ome cases to destroy the organic matter, and resolution of the evaporated ass in hydrochloric acid causes a reduction of some of the ferric salt.

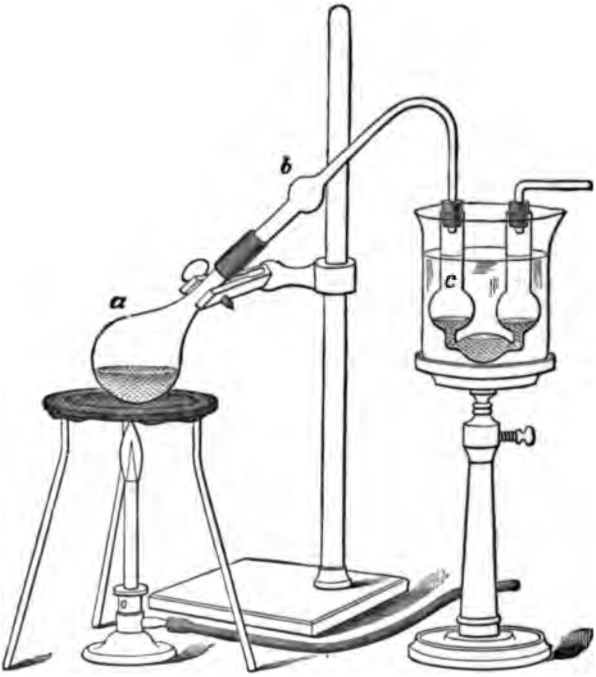
DETERMINATION OF MANGANESE DIOXIDE.

Many manganiferous iron ores contain manganese in a higher state f oxidation than the protoxide, and the determination of the excess of xygen is often necessary. All ores of this character when treated with ydrochloric acid evolve chlorine gas, which is easily recognized by its yelowish-green color and peculiarly irritating odor. The reaction by which hlorine is liberated is $MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$, or each olecule of manganese dioxide = 87 corresponds to 2 molecules of hlorine = 70.90. This reaction is the basis of Bunsen's method for the stimation of the amount of manganese dioxide in manganese ores, which onsists in driving the liberated chlorine into a solution of potassium odide, and determining the amount of iodine set free by starch and hypolphite solution. When the method given on page 68 for determining lphur in steel is in use, the solutions employed in carrying out that ethod (with the exception of the iodine in potassium iodide) can be used this, or they may be prepared by the directions there given, for use in is method.

Bunsen's Method.

Weigh from .5 gramme to 1 gramme of the finely ground ore and place it in the flask *a*, Fig. 95, pour in 10 c.c. strong hydrochloric acid, connect the bent tube *b* quickly by means of a piece of rubber tubing, and heat the flask gently at first and finally to boiling to drive all the chlorine over into the tube *c*, which contains a strong solution of pure potassium iodide free from iodate. This tube is placed in ice-water. When all the chlorine has been expelled from the flask *a* and absorbed in *c*, detach the latter, wash its contents into a large dish, add a little starch solution, and run in the hyposulphite until the blue color just vanishes. If, as in the example given on page 71, 1 c.c. of the hyposulphite solution is equal to .01267 gramme of iodine, and 1 equivalent of chlorine = 35.45 replaces 1 equivalent of iodine = 126.85 in the potassium iodide, 1 c.c. of the hyposulphite

FIG. 95.



solution would be equal to (126.85 : 35.45 : : .01267 : .003541) .003541 gramme of chlorine; and, as 1 equivalent of manganese dioxide = 87 is equal to 2 equivalents of chlorine = 70.90, 1 c.c. of the hyposulphite would be equal to (70.90 : 87 : : .003541 : .004345) .004345 gramme manganese dioxide.

Determination by Ferrous Sulphate.

In most laboratories, however, it is generally more convenient to estimate the amount of manganese dioxide in an ore by determining its oxidizing power on a solution of ferrous salt. The reaction is $2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$, or 2 equivalents of iron = 112 are equal to 1 equivalent of manganese dioxide = 87. Grind in an agate or Wedgwood mortar about 10 or 15 grammes of ferrous sulphate or ferrous-ammonio sulphate, and weigh out two portions, one of 2 grammes and one of from 3 to 8 grammes, according to the quality of the manganese ore. One gramme of pure manganese dioxide would oxidize 1.2874 grammes of iron, equal to nearly 6.5 grammes of ferrous sulphate, or more than 9 grammes of ferrous-ammonio sulphate. Transfer the 2-gramme portion to the dish, add a large amount of water and about 5 c.c. hydrochloric acid, and pour in 3 grammes of zinc dissolved in 10 c.c. sulphuric acid diluted with enough water to dissolve the zinc sulphate completely. Titrate with the standard solution of potassium permanganate or bichromate in the usual way, and calculate the amount of iron in 1 gramme of the ferrous salt used. Weigh into the flask A (Fig. 93, page 222) 1 gramme of the finely ground ore, and add to it the larger portion of the ferrous salt previously weighed out. Connect the flask as shown, and pass in a current of carbonic acid until the air has been driven out. Now pour into the flask A, by means of a small funnel attached to B, 10 c.c. hydrochloric acid and 30 c.c. water, reconnect the carbonic acid apparatus, and while the current of carbonic acid is passing dissolve the ore, heating the flask, and shaking it from time to time as necessary. When the ore is all decomposed, stop the current of carbonic acid for a moment, remove the light, and allow the water in E to flow back into the flask A. Transfer the solution to the dish, add 3 grammes zinc dissolved in sulphuric acid, and titrate with the standard solution. From the titration of the ferrous salt calculate the amount of iron in the amount used in the solution of the ore, and subtract from this the amount found by this last titration; the difference is the weight of iron oxidized by the chlorine liberated from the manganese dioxide in the ore. Then, as 112 parts of iron correspond to 87 parts of manganese dioxide, multiply the above weight of iron by 87 and divide by 112, and the result is the weight of manganese dioxide in the ore.

The total manganese having been determined by one of the methods previously given, subtract from it the amount of manganese as manganese dioxide (found by multiplying the weight ot manganese dioxide by .63218), and calculate the difference to manganous oxide by multiplying by 1.2909.

DETERMINATION OF SILICA, ALUMINA, LIME, MAGNESIA, MANGANESE OXIDE, AND BARYTA.

Treatment of iron ores with hydrochloric acid leaves a residue which only in very rare instances consists of silica alone, being usually silicates of aluminum, calcium, and magnesium, mixed with an excess of silica. These silicates are often much more complicated, and contain, besides the substances enumerated above, ferrous oxide, soda, potash, and manganese oxide. With these silicates are occasionally found titanic acid, titaniferous iron, chrome iron ore, barium sulphate, and ferrous sulphide, besides organic matter, and sometimes graphite. As this residue must be fused with sodium carbonate in order to decompose it, and the introduction of sodium salts into the main solution is not desirable, the two portions of the ore (the soluble and the insoluble in hydrochloric acid) should be analyzed separately.

Place 1 gramme of ore in a No. 1 beaker, add 15 c.c. hydrochloric acid, cover with a watch-glass, and digest at a gentle heat until the ore appears to be quite decomposed, add a few drops of nitric acid, heat until the action has ceased, and then wash off the cover with a fine jet of water and evaporate to dryness. Redissolve in hydrochloric acid, and evaporate to dryness a second time to render all the silica insoluble. Redissolve in 10 c.c. hydrochloric acid and 30 c.c. water, filter, transfer all the residue to the filter (a small ashless filter) with a fine jet of cold water, using a "policeman" to detach any adhering particles from the beaker, and wash the filter with a little hydrochloric acid and plenty of cold water. Allow the filtrate and washings to run into a No. 5 beaker, and ignite and weigh the residue as "Insoluble Silicious Matter."

Add to the insoluble matter in the crucible about ten times its weight of pure dry sodium carbonate and fuse it. Run the fusion well up on the sides of the crucible, cool, and dissolve in hot water. Transfer to a platinum dish, dissolve any particles adhering to the crucible in hydrochloric acid, and add this to the solution in the dish. Acidulate with hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid and water, evaporate to dryness a second time to render silica insoluble, then pour into the dish 5 c.c. hydrochloric acid and 15 c.c. water, and stand it in a warm place for some time. Dilute with about 20 c.c. water, filter on a small ashless filter, wash well with hot water, receiving the filtrate and washings in a small beaker, dry, ignite, and weigh. Treat the ignited precipitate with hydrofluoric acid and a drop or two of sulphuric acid, evaporate to dryness, ignite, and weigh again. The difference between the two weights is silica. If the difference between the last weight and the weight of the empty crucible is more than a milligramme or two, the residue must be examined and its nature determined. This residue may consist of titanic acid, barium sulphate, alumina, or sodium sulphate (from imperfect washing of the silica). If it is titanic acid or alumina, the weight must be added to the weights of the alumina, etc.

Return the filtrate from the silica to the dish in which it was previously contained, heat to boiling, add a few drops of bromine-water and an excess of ammonia, boil until it smells but faintly of ammonia, filter on a small ashless filter, wash well with hot water, dry, ignite, and weigh as alumina, etc. Besides alumina this precipitate may contain titanic acid, chromium sesquioxide, ferric oxide, manganous oxide, and phosphoric acid.

Return the filtrate from this precipitate to the dish, evaporate down to about 100 c.c., add ammonium oxalate and ammonia, boil for a few minutes, allow the precipitate to settle, filter on a small ashless filter, ignite finally for five minutes over a blast-lamp, and weigh as lime. To the filtrate from the lime add microcosmic salt and about one-third the volume of the solution of ammonia, cool in ice-water, stir vigorously several times, and allow to stand overnight so that the precipitated ammonium-magnesium orthophosphate may settle properly, filter, wash with water containing one-third its volume of ammonia and about 100 grammes of ammonium nitrate to the litre, ignite carefully, and weigh. Dissolve the precipitate in the crucible in a little water containing from 5 to 10 drops hydrochloric acid, filter through a small ashless filter, which dry, ignite, and weigh. The difference between the two weights is magnesium pyrophoshate, which, multiplied by .36212, gives the weight of magnesia.

When barium has been shown to exist in the ore, as noted on page 236, heat the filtrate from the "Insoluble Silicious Matter" to boiling, add a few drops of sulphuric acid, boil for a few minutes to allow the precipitate to settle, filter on a small ashless filter, allowing the filtrate and washings to run into a No. 5 beaker, dry, ignite, and weigh as barium sulphate, which, multiplied by .65648, gives the weight of barium oxide.

To the cold filtrate from the barium sulphate add ammonia until the solution is nearly neutralized, then add a solution of ammonium carbonate until a slight permanent precipitate is formed which fails to dissolve after vigorous stirring, and redissolve this by the careful addition of hydrochloric acid, drop by drop, stirring well, and allowing the solution to stand for a short time after each addition of hydrochloric acid. As soon as the solution clears, add a solution of ammonium acetate, made by slightly acidulating 5 c.c. of ammonia by acetic acid, dilute to about 600 c.c. with boiling water, and boil for a few minutes. Allow the precipitate to settle, decant the clear liquid through a large washed filter, pour the precipitate on the filter, and wash it two or three times with boiling water. With the aid of a platinum spatula return the precipitate to the beaker in which the precipitation was made, dissolving any portion remaining on the filter or adhering to the spatula in dilute hydrochloric acid, allowing the acid to run into the beaker containing the precipitate. Wash the filter thoroughly with cold water, and evaporate the solution and washings to dryness. Redissolve in dilute hydrochloric acid, filter into a large platinum dish, dilute with hot water,[*] heat to boiling, and add a slight excess of ammonia. Boil for a few minutes to make the precipitate granular and expel the excess of ammonia, and filter on an ashless filter (using the filter-pump and cone, page 27, with very slight pressure, if practicable). Dissolve any particles of the precipitate adhering to the dish in a very few drops of hydrochloric acid, heating the bottom of the dish slightly, wash off the rod and cover, and wash down the sides of the dish with hot water, add a slight excess of ammonia, heat gently until the precipitate of ferric hydrate separates, wash this onto the filter, and wash the precipitate thoroughly with hot water. Dry the filter and precipitate carefully, transfer the latter to a weighed crucible, burn the filter in a wire, add the ash to the precipitate, and heat the crucible, keeping it carefully covered, and raising the heat very gradually to expel the last traces of moisture from the precipitate of ferric hydrate. Finally heat the crucible to bright redness, and then to the highest temperature of the blast-lamp for from five to ten minutes. Cool, ignite, and weigh as ferric oxide + alumina + phosphoric acid (+ titanic acid + chromic oxide + arsenic acid).

Add the filtrate and washings from the acetate precipitation to those from the precipitation by ammonia, evaporate down to about 200 c.c. in a platinum dish, filter off any slight precipitate of ferric oxide (which must be ignited, weighed, and the weight added to that of the ferric oxide, etc.), add from 20 to 30 drops of acetic acid, heat to boiling, and pass a current of hydrogen sulphide through the solution for fifteen or twenty minutes, keeping the solution hot during the passage of the gas. Filter off the precipitated copper, zinc, nickel, and cobalt sulphides, wash with hydrogen sulphide water containing a little free acetic acid, and to the filtrate add excess of ammonia and ammonium sulphide. Allow the precipitated manganese sulphide to settle, decant the clear, supernatant liquid through a filter, but before pouring the precipitate on the filter remove the beaker containing the filtrate and substitute a clean beaker, as the precipitate is almost certain at first to run through the filter. Wash the precipitate and filter with water containing a little ammonium sulphide, add the clear filtrate and washings together, and stand them aside. Dissolve the precipitate of manganese sulphide on the filter in dilute hydrochloric acid, and wash the filter thoroughly with hot water, receiving the solution and washings in a small beaker. Heat to boiling to expel hydrogen sulphide, and, when the excess is driven off, destroy the last traces with a little bromine-water, transfer the solution to a platinum dish, and precipitate by microcosmic salt and ammonia as directed on page 110. Filter, wash, ignite, and weigh as manganese pyrophosphate, which, multiplied by .50011, gives the weight of manganous oxide.

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[*] The distilled water used in the complete analysis of iron ores should never be heated in glass vessels for any length of time, as glass is sensibly attacked by it. An experiment in which distilled water free from residue was heated for twelve hours in a Bohemian flask showed that the water dissolved 52 milligrammes of solid matter to the litre, of which 26 milligrammes were silica. The water should always be heated in platinum or porcelain dishes, or in tin-lined copper flasks. For convenience, the water may be poured into the washing-flasks for immediate use.

Acidulate the filtrate from the manganese sulphide with hydrochloric acid, boil off all the hydrogen sulphide, filter from the sulphur deposited by this operation into a platinum dish, add an excess of ammonia and ammonium oxalate, filter, ignite, and heat at the highest temperature of the blast-lamp for fifteen minutes, cool, and weigh as lime.

Precipitate the magnesia in the filtrate as directed on page 238, and determine the weight of magnesium pyrophosphate, which, multiplied by .36212, gives the weight of magnesia.

By adding the elements determined in the insoluble portion to the similar ones in the soluble portion, we get the total amounts of each in the ore. Thus, we have from the above analysis silica, ferric oxide + alumina + phosphoric acid + chromic oxide + titanic acid + arsenic acid, manganese oxide, lime, and magnesia, and it becomes, of course, necessary to calculate properly the iron in its different states of oxidation and to determine the amount of alumina in the ore. It is much more accurate to determine in separate portions of the ore the amounts of phosphoric acid, arsenic acid, chromic oxide, ferric oxide, and titanic acid than to attempt to make the separation in the precipitate obtained in this portion. Therefore, knowing the amounts of these substances, the ferric oxide from the volumetric determination of iron, as previously described, and the amount of each of the others as found by one of the methods given, add together the weights of the ferric oxide, the phosphoric acid, the chromic oxide, the titanic acid, and the arsenic acid in one gramme of the ore, and subtract the sum from the weight of the precipitate obtained in the above analysis, the result is the weight of alumina in one gramme of the ore.

Iron may exist in an ore in several conditions, as Fe_2O_3, as FeO, as FeS_2, as $FeAs_2$, etc. While it may not always be possible to determine the exact conditions in which it exists, the rule usually followed is, after subtracting from the sulphur existing as sulphides (page 227) the amount necessary to form copper sulphide, nickel sulphide, etc., to calculate the remainder as FeS_2 by multiplying the weight of sulphur by 1.87336. The weight of sulphur subtracted from this gives the weight of iron in the FeS_2. Now from the weight of $FeAs_2$ subtract the weight of arsenic, and the result is the weight of iron existing as iron in the $FeAs_2$.* Add the iron in the FeS_2 to the iron in the $FeAs_2$, and subtract this weight from the iron found as ferrous oxide, the remainder calculated to ferrous oxide is the amount of ferrous oxide in the ore. Subtract the total amount of iron found originally by titration to exist as ferrous oxide from the total iron found in the ore, and calculate the remainder to ferric oxide.

When an iron ore contains only a very small amount of manganese, the acetate separation may be omitted in the method as given above, which simplifies and shortens the operation very materially. In this event transfer the filtrate from the insoluble silicious matter at once to a large platinum dish, heat to boiling, add a few c.c. of bromine-water and then excess of ammonia, boil, filter the ferric oxide, etc., on an ashless filter, dry, ignite, and weigh, as described above. The manganese will be in the precipitate after ignition as manganoso-manganic oxide, and the amount calculated from the determination of manganese made in a separate portion of the ore must be subtracted from the weight of the above precipitate in calculating the amount of alumina.

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* All the weights, of course, are calculated to one gramme of ore.

The lime and magnesia are determined in the filtrate from the ferric oxide, etc., provided, of course, that the ore contains only minute amounts of nickel, copper, etc.

The same general method described above is applicable when the ore contains quite a large amount of titanic acid, so much, in fact, as to cause the cloudiness in the filtrate from the insoluble silicious matter, as noted on page 228. Whenever an acetate separation is necessary in an ore of this character, the precipitate must be filtered on an ashless filter, and this, as well as the filter containing any insoluble matter from the resolution of the acetate precipitate, must be ignited and examined for titanic acid by treating the residue with hydrofluoric and sulphuric acids, heating to redness, fusing with sodium carbonate, dissolving in hydrochloric acid and water, and precipitating by ammonia. The precipitate so obtained is to be filtered, ignited, and the weight added to that of the ferric oxide, etc. Ilmenite even, when very finely ground in an agate mortar, is frequently capable of being almost entirely decomposed by hydrochloric acid, and when this is the case it is of advantage to use this method of analysis. It may be necessary, however, under certain circumstances to decompose the ore at the start by fusing with potassium bisulphate. To carry out this method, place 1 gramme of the ore, which has been ground as fine as possible in an agate mortar, in a large platinum crucible, add 10 grammes of pure potassium bisulphate,* and heat the crucible, carefully covered, over a very low light until the bisulphate is melted. It is necessary to watch this operation most carefully, for the bisulphate has a strong tendency to boil over, and only unremitting attention on the part of the analyst will prevent the loss of the analysis. It is well at the start to stand by the crucible and raise the lid slightly at very short intervals to watch the condition and progress of the fusion. The lid should be held just over the crucible and in a horizontal position, otherwise the particles which have spirted on it from the mass in the crucible may run to the edge of the lid and, when the latter is replaced, down the outside of the crucible. Raise the heat very gradually, keeping the mass just liquid and the temperature at the point at which slight fumes of sulphuric anhydride are given off when the lid is raised, until the bottom of the crucible is dull red. When the ore is completely decomposed, remove the light, take off the lid of the crucible, and incline the latter at such an angle that the fused mass may run together on one side of the crucible and as near the top as possible. Allow it to cool in this position; when cold it is easily detached from the crucible. Place the crucible and lid in a No. 4 beaker half full of cold water, and the fused mass in the little basket, as shown in Fig. 81, page 168. Pour into the beaker enough strong aqueous solution of sulphurous acid to raise the liquid to the top of the basket, and allow the fusion to dissolve, which may require twelve hours. Wash with a jet of cold water, and remove the basket, the crucible, and the lid, stir the liquid, which should smell strongly of sulphurous acid, and allow the insoluble matter to settle. Filter on an ashless filter, wash well with cold water, dry, ignite, and weigh. Treat with hydrofluoric acid and 2 or 3 drops of sulphuric acid, evaporate to dryness, ignite, and weigh. The difference between the weights is silica. If any appreciable residue remains in the crucible, fuse with a little sodium carbonate, treat with sulphuric acid, and add to the main filtrate. To the main filtrate, which should be quite colorless and smell strongly of sulphurous acid, add a clear filtered solution of 20 grammes of sodium acetate and one-sixth of its volume of acetic acid (1.04 sp. gr.), heat to boiling, and boil for a few minutes. Allow the precipitate to settle, filter on an ashless filter, wash thoroughly with hot water containing one-sixth its volume of acetic acid, and finally with hot water, dry, ignite, and weigh as titanic acid. This precipitate, however, may not be quite pure, as small amounts of ferric oxide and alumina may be carried down with it. The best plan to pursue is to fuse with sodium carbonate, dissolve in water, filter, wash, dry, and fuse the insoluble sodium titanate, etc., with sodium carbonate, treat the cooled mass in the crucible with sulphuric acid, and precipitate and determine the titanic acid as directed above. The two filtrates from the treatment of the first precipitate of titanic acid may contain a little ferric oxide and alumina. To recover this, boil down the last filtrate until the greater part of the sulphurous acid has been driven off, add bromine-water to oxidize the iron, acidulate the aqueous filtrate from the sodium carbonate fusion with sulphuric acid, add it to this solution, boil the united solutions down in a platinum dish to a convenient volume, and add a slight excess of ammonia. Boil the solution until it smells faintly but decidedly of ammonia, filter, and wash slightly. Redissolve the precipitate in hydrochloric acid, and reprecipitate by ammonia, filter, wash, ignite, and weigh as ferric oxide alumina, to be added to the main precipitate. Boil the main filtrate and washings down in a large platinum dish after adding enough bromine-water to oxidize all the iron, add hydrochloric acid from time to time when necessary to keep the iron in solution, and, when reduced to a convenient bulk, nearly neutralize by ammonia, and boil. Filter, and wash the precipitate two or three times, redissolve and reprecipitate by ammonia, filter, wash, dry, ignite, and weigh as ferric oxide + alumina + phosphoric acid. Fuse this precipitate for a long time and at a high temperature with sodium carbonate, dissolve in water, wash by decantation, redissolve the residue of ferric oxide, etc., in hydrochloric acid, and determine the iron by titration. The alumina is obtained by difference, the phosphoric acid being determined in a separate portion. In the filtrate from the ferric oxide + alumina + phosphoric acid determine manganese, lime, and magnesia in the usual way.

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* See page 49.

DETERMINATION OF SILICA.

When silica alone is wanted in an ore a more rapid method is sometimes desirable. In this case dissolve 1 gramme of the ore in hydrochloric acid, evaporate to dryness, redissolve in dilute hydrochloric acid, filter on an ashless filter, wash, dry, ignite, and weigh the insoluble silicious matter. Treat this in the crucible with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite, and weigh. It is evident now that if the insoluble silicious matter contains calcium, magnesium, potassium, or sodium, the loss of weight, which in the absence of these elements would represent the silica volatilized as silicon tetrafluoride, will be decreased by the amount of sulphuric acid which, uniting with these elements, remains as a part of the residue in the crucible. It is a simple operation, however, to fuse this residue with sodium carbonate, dissolve in water, acidulate with hydrochloric acid, heat to boiling, add solution of barium chloride and filter off, and weigh the precipitated barium sulphate. This being accomplished, calculate the amount of sulphuric anhydride, and add its weight to the loss by volatilization. The result is the weight of silica. When the ore contains appreciable amounts of barium sulphate this method is not admissible.

Separation of Alumina from Ferric Oxide.

Besides the indirect method for determining alumina, it is sometimes necessary or convenient to make a direct separation. The method usually taken, the iron and alumina being in solution in hydrochloric acid, is as follows. Add to the solution about five times the weight of the oxides, of citric acid (tartaric acid may be used, but, as it is liable to contain alumina, citric acid is preferable) and excess of ammonia. If the solution remains clear, heat to boiling, and add a fresh solution of ammonium sulphide until all the iron is precipitated. If the solution does not remain clear on the addition of ammonia, acidulate with hydrochloric acid, add more citric acid, and then excess of ammonia. Allow the ferric sulphide to settle, decant the clear liquid through a washed filter, throw the precipitate on the filter, and wash it well with water containing ammonium sulphide and ammonium chloride, changing the beaker into which the washings run before each addition of wash-water, and keeping the funnel well covered with a watch-glass. Unite the filtrate and washings, acidulate with hydrochloric acid, boil until the precipitated sulphur agglomerates, filter into a platinum dish, and evaporate to dryness. Heat carefully until the ammonium chloride is volatilized and there remains in the dish a mass of carbonaceous matter from the decomposition of the citric acid. The expulsion of the last traces of water from the ammonium chloride nearly always causes loss by spirting, but the difficulty may be entirely avoided by placing the dish in one of the holes of the air-bath overnight, after having lightly coated the upper edge of the dish with paraffine or grease to prevent the ammonium chloride from creeping over the top. This long heating expels the last traces of water without the least disturbance, and the dish may at once be placed over a Bunsen burner, and the mass in it decomposed without fear of loss. Transfer the carbonaceous matter to a crucible, wiping out the dish carefully with filter-paper, and placing these in the crucible also. Burn off the carbon in the crucible, fuse the residue with sodium carbonate and a little sodium nitrate, treat with water, transfer to a platinum dish, dissolve any adhering particles in the crucible in hydrochloric acid, add this to the solution in the dish, with enough hydrochloric acid to acidulate it, heat to boiling after diluting, add a slight excess of ammonia, boil until the solution smells but faintly of ammonia, filter, wash thoroughly, ignite, and weigh as alumina. This precipitate will contain any phosphoric and titanic acids that may have been in the original solution. They may be separated by the methods given previously. It is liable to contain also a little iron, which is almost invariably held in solution by the ammonium sulphide.

Dissolve the precipitate of ferrous sulphide on the filter in dilute hot hydrochloric acid, allow the solution and washings to run into the beaker in which the precipitation was made, add a little nitric acid, evaporate to dryness, redissolve in as little dilute hydrochloric acid as possible, filter into a platinum dish, dilute, precipitate by ammonia, filter, wash, dry, ignite, and weigh as ferric oxide.

Rose * suggested the method based on the solubility of alumina in caustic potash or soda. When the iron and alumina are in solution, evaporate in a platinum dish until syrupy, add a strong solution of caustic soda or potash until the solution is strongly alkaline, and then add a large excess of the precipitant, and boil for ten or fifteen minutes; or, pour the nearly neutral solution of the chlorides into a boiling solution of caustic soda or potash in a platinum or silver dish, in a thin stream, stirring continually. Filter, wash with hot water, carefully acidulate the filtrate with hydrochloric acid, and precipitate the alumina by ammonia, filter, wash, dissolve in hydrochloric acid, evaporate to dryness to get rid of silica, redissolve, filter, and determine as usual. As the ferric oxide precipitated by caustic soda or potash always contains alkali,

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* Chimie Anal. Quant. (French ed.), page 148.

it must be dissolved in hydrochloric acid, precipitated by ammonia, filtered, and weighed in the usual manner.

Rose also suggested fusing the finely ground ignited oxides in a silver crucible with potassium or sodium hydrate; but this method, as well as the other, is open to the objection that it is almost impossible to get caustic soda or potash that does not contain alumina, and generally there is more in the reagent than in the ore.

Rivot suggested the following method. After weighing the ignited iron and aluminum oxides, grind them very fine, weigh them, and place in a porcelain or platinum boat. Place the boat in a porcelain or platinum tube, and heat to redness in a current of hydrogen gas until no more water appears to come off. Replace the hydrogen by a stream of hydrochloric acid gas, reheat the tube, and continue the current as long as ferric chloride is given off. Remove the boat, and, if the residue is not white, repeat the operation. Weigh the remaining alumina, and calculate from the amount of the oxides used the total amount in the ore.

Rose modified this method by substituting a crucible and tube for the boat, etc. The apparatus as he used it is the same as that described for the determination of manganese as sulphide (page 112).

Wöhler suggested the method of separating iron and alumina by boiling the nearly neutral solution with an excess of sodium hyposulphite. The following modification of this method* appears to give excellent results, and has the advantage of doing away with a subsequent separation of phosphoric acid in those cases in which it has not been determined in another portion. The ferric oxide and alumina from 1 gramme of ore being in solution in hydrochloric acid, dilute to 400 or 500 c.c. with cold water, and add ammonia until the solution becomes dark red in color, but contains no precipitate. Now add 3.3 c.c. hydrochloric acid (1.2 sp. gr.) and 2 grammes sodium phosphate, dissolved in water and filtered; stir until the precipitate formed is dissolved and the solution becomes perfectly clear again. Add now 10 grammes of sodium hyposulphite, dissolved in water and filtered if necessary, and 15 c.c. of acetic acid (1.04 sp. gr.), heat to boiling, boil fifteen minutes, filter as rapidly as possible on an ashless filter, wash thoroughly with hot water, dry, ignite in a porcelain crucible, and weigh as aluminum phosphate, which, multiplied by .41847, gives the weight of alumina. It is necessary in burning off the precipitate to raise the heat very carefully until all the carbon has been burned off, as the aluminum phosphate may fuse and make it almost impossible to burn off the carbon.

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* Communicated to the author by Mr. S. Peters in 1879.

DETERMINATION OF NICKEL, COBALT, ZINC, AND MANGANESE.

For the determination of these elements use 3 grammes of ore, dissolve in hydrochloric acid, add a little nitric acid or potassium chlorate to oxidize any ferrous oxide in the ore, evaporate to dryness, redissolve in hydrochloric acid, and evaporate a second time if necessary to get rid of all nitric acid. As noted on page 233, when the ore contains much organic matter, dissolve in hydrochloric acid (if there is much gelatinous silica, evaporate to dryness or the filtration will be much retarded), filter, add nitric acid or potassium chlorate, evaporate to dryness, redissolve in hydrochloric acid, and evaporate a second time if necessary, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, filter into a No. 6 beaker, and proceed exactly as directed for the determination of manganese in iron and steel (page 108 *et seq.*) until the precipitate by hydrogen sulphide is obtained and filtered off. Determine the manganese, if desired, in the filtrate, as directed on page 110, and calculate to manganous oxide.

Dry and ignite the precipitated sulphides of nickel, cobalt, zinc, copper, lead, etc., in a porcelain crucible, transfer to a small beaker, and dissolve in hydrochloric acid, with the addition of a drop or two of nitric acid. Evaporate to dryness, redissolve in from 10 to 20 drops of hydrochloric acid, dilute to 50 or 60 c.c., heat to boiling, and pass a current of hydrogen sulphide through the boiling solution. Filter off he precipitated sulphides of copper, lead, etc., and wash with water ontaining hydrogen sulphide. Evaporate the filtrate, which contains nly nickel, cobalt, and zinc, to dryness. To the dry salts in the bottom f the beaker add 2 drops of strong hydrochloric acid, dilute to 150 c.c. vith cold water, and pass hydrogen sulphide through the solution until t is thoroughly saturated with the gas. If a white precipitate forms, it s zinc sulphide. Allow to stand several hours, filter, wash with hydrogen sulphide water (the zinc sulphide has a tendency to pass through he filter, and consequently the beaker into which the filtrate is received must be changed before the precipitate is poured on the filter), dry, and ignite the precipitate. Heat it several times with ammonium carbonate to drive off any sulphuric acid that may have been formed by the ignition, cool, and weigh as zinc oxide. The precipitate is greenish white while hot and yellowish white when cold. If it should carry down a little cobalt from the solution, the ignited precipitate of zinc oxide is green when cold. Pass hydrogen sulphide through the filtrate from the zinc sulphide again, and, if no further precipitate appears, add a few drops of a solution of .5 gramme of sodium acetate in 10 c.c. water. If this occasions a white precipitate, filter it off, after standing, as in the first instance; but if the precipitate is black (as it is almost certain to be if the instructions given above are strictly followed), add the rest of the sodium acetate solution, heat the solution to boiling, while the passage of the hydrogen sulphide is continued, allow the precipitate to settle, filter, ignite, and treat it as directed for the separation and determination of nickel and cobalt (page 184 *et seq.*).

DETERMINATION OF COPPER, LEAD, ARSENIC, AND ANTIMONY.

Treat 10 grammes of the finely ground ore with 50 c.c. hydrochloric acid, add a little potassium chlorate from time to time, and increase the heat gradually until the ore is perfectly decomposed. Dilute, filter into a No. 5 beaker, deoxidize with ammonium bisulphite, as directed on page 81, drive off the excess of sulphurous acid, and pass hydrogen sulphide through the solution for fifteen or twenty minutes. Allow the solution to stand for some hours until the precipitate has settled completely and the solution smells but faintly of hydrogen sulphide. Filter on a thin felt on the Gooch crucible or small cone, wash with cold water, and suck dry. Transfer the felt and precipitate to a small beaker, using a little asbestos wad in the forceps to wipe off any adhering precipitate from the large beaker and the crucible or cone, and digest it with a few c.c. of a colorless solution of potassium sulphide. Dilute to about 100 c.c., filter on another felt, and wash with water containing a little potassium sulphide. The solution contains the arsenic and antimony sulphides dissolved in potassium sulphide, while the copper and lead sulphides remain on the felt. Return the felt with the precipitate to the beaker from which they were filtered, and digest with hydrochloric acid, with the addition of nitric acid, until all the black sulphides are dissolved, dilute with a little hot water, and filter. Evaporate the filtrate, after adding a few drops of sulphuric acid, until fumes of sulphuric anhydride are evolved, allow to cool, dilute with 25 c.c. cold water, add one-half its bulk of alcohol, allow to settle, filter the precipitated lead sulphate on the Gooch crucible, wash with alcohol and water, heat carefully over a low light, and weigh. Treat the precipitate on the felt under a slight pressure with a strongly ammoniacal solution of ammonium citrate, to dissolve the lead sulphate, wash with hot water, and weigh. The difference between the two weights is lead sulphate, which, multiplied by .68298, gives the weight of lead, or, multiplied by .78879, gives the weight of lead sulphide.

Evaporate the filtrate from the lead sulphate until the alcohol is driven off and the solution reduced to a convenient bulk, transfer to a platinum crucible, and precipitate the copper on the small platinum cylinder by the battery (Fig. 88). The weight of copper, multiplied by 1.25284, gives the weight of cuprous sulphide.

Acidulate the filtrate of potassium sulphide containing arsenic and antimony in solution with hydrochloric acid, and allow to stand in a warm place until all the hydrogen sulphide has been driven off and the arsenic and antimony sulphides mixed with the excess of sulphur have settled completely. Filter on a thin felt, wash with warm water, then with alcohol, and finally with carbon disulphide, to dissolve the excess of sulphur. Transfer the felt and precipitate to a small beaker, add 5 c.c. hydrochloric acid and a few crystals of potassium chlorate. Digest at a low temperature for some time, adding occasionally a small crystal of potassium chlorate, finally heat a little, but not to a sufficiently high degree to fuse any little particles of separated sulphur, keeping the liquid always full of the products of decomposition of the potassium chlorate. When all the arsenic and antimony sulphides are dissolved, dilute with about 20 c.c. of warm water, and add a few small crystals of tartaric acid to keep the antimony in solution. Filter from the asbestos, using as little wash-water as possible in order to keep down the volume of the solution, add a slight excess of ammonia to the filtrate, and if it remains clear 5 c.c. of magnesia-mixture and one-third the volume of the solution of ammonia. Cool in ice-water, and stir vigorously from time to time to precipitate the ammonium-magnesium arsenate.

Allow to stand overnight, filter, and determine the arsenic as directed on page 195. If the acid solution above mentioned becomes cloudy upon the addition of ammonia, acidulate carefully with hydrochloric acid, and add a little more tartaric acid. Then proceed as above directed. The weight of arsenic calculated from the amount of magnesium pyroarsenate, multiplied by 1.373, gives the weight of ferrous arsenide.

Acidulate the filtrate from the ammonium-magnesium arsenate, which contains none of the washings, with hydrochloric acid, so that the solution is just acid to test-paper, dilute with hot water to about 250 c.c., and pass hydrogen sulphide into the solution, heating it gradually to boiling. Drive off the excess of hydrogen sulphide with a current of carbonic acid, filter on a felt in the Gooch crucible, wash with water, alcohol, and finally with carbon disulphide to dissolve any free sulphur, dry carefully, heat to a temperature slightly above 100° C., and weigh as antimony trisulphide. For the very small amounts of antimony that are found in iron ores this method is sufficiently exact. The weight of antimony trisulphide, multiplied by .71390, gives the weight of antimony.

DETERMINATION OF THE ALKALIES.

As a rule, the alkalies in iron ores are found exclusively in the insoluble silicious matter, and when the sum of the weights of the silica, alumina, etc., lime, and magnesia in the insoluble silicious matter falls much below the weight of the latter, it is always well to look for alkalies.

Dissolve 3 grammes of the ore in hydrochloric acid, evaporate to dryness, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, and filter into a platinum dish. Ignite the insoluble residue, treat it in the crucible with hydrofluoric acid and from 10 to 30 drops sulphuric acid, evaporate down until the sulphuric acid is driven off, dissolve in water with a little hydrochloric acid if necessary, transfer to a small platinum dish, dilute to 100 c.c., heat to boiling, and add excess of barium hydroxide. Boil for a few minutes, and filter from the alumina, etc., into another platinum dish. Evaporate the filtrate to dryness, treat the residue with a little water, heat to boiling and add ammonium carbonate to precipitate the barium, filter into another platinum dish, evaporate to dryness, and heat to dull redness. Dissolve in a few c.c. of water, and filter into a weighed crucible.

Evaporate very low, and, if nothing separates out, add a few drops of hydrochloric acid, evaporate to dryness, heat to very dull redness, cool, and weigh as potassium chloride + sodium chloride. To the residue in the crucible add a little water, in which the residue should dissolve perfectly, and a solution of platinic chloride. Evaporate down in the water-bath until the mass in the crucible solidifies upon cooling, add a little water to dissolve the excess of platinic chloride, and then an equal volume of alcohol. Filter on a Gooch crucible, wash with alcohol until the filtrate runs through perfectly colorless, dry at 120° C., and weigh as potassium-platinic chloride. This weight, multiplied by .19395, gives the weight of potash. Then multiply the weight of potassium-platinic chloride by .30696, which gives the weight of potassium chloride. Subtract this from the weight of potassium chloride + sodium chloride previously obtained, and the difference is the weight of sodium chloride, which, multiplied by .53077, gives the weight of soda.

To the filtrate from the insoluble silicious matter add an excess of ammonia, rub a little grease or paraffine on the edge of the dish, and evaporate the mass to dryness. This will render the ferric oxide very compact and granular. Dilute with hot water, add a few drops of ammonia, filter into another platinum dish, add a few drops of sulphuric acid, evaporate to dryness, and ignite to drive off all the ammonia salts. Then proceed exactly as directed for the determination of the alkalies in the insoluble silicious matter. The alkalies in the insoluble silicious matter may also be determined by J. Lawrence Smith's method of fusion with calcium carbonate and ammonium chloride, as directed farther on.

The ammonium chloride, which is so troublesome in alkali determinations, may be decomposed * very easily by evaporating the solution down very low, transferring to a tall beaker or flask, and heating with a large excess of nitric acid,—3 or 4 c.c. nitric acid to every gramme of ammonium chloride supposed to be present. The decomposition takes place at a temperature below the boiling-point of water, and when the action seems to be over, transfer to a porcelain dish, and evaporate to dryness after adding a few drops of sulphuric acid. Dissolve in water, filter into a platinum dish, and proceed with the analysis in the usual way.

DETERMINATION OF CARBONIC ACID.

Weigh 3 grammes of finely ground ore into the flask A (Fig. 96), and connect the apparatus in the manner shown in the sketch. L, L are tubulated bottles for forcing a current of air through the apparatus. The air is deprived of any carbonic acid which it may contain by passing through the tube M, which is filled with caustic potash. M is connected with the bulb-tube B by the tube N, a piece of rubber tubing over the slightly tapering end making an air-tight connection with B. O is a condenser and serves to condense the steam and acid from the flask

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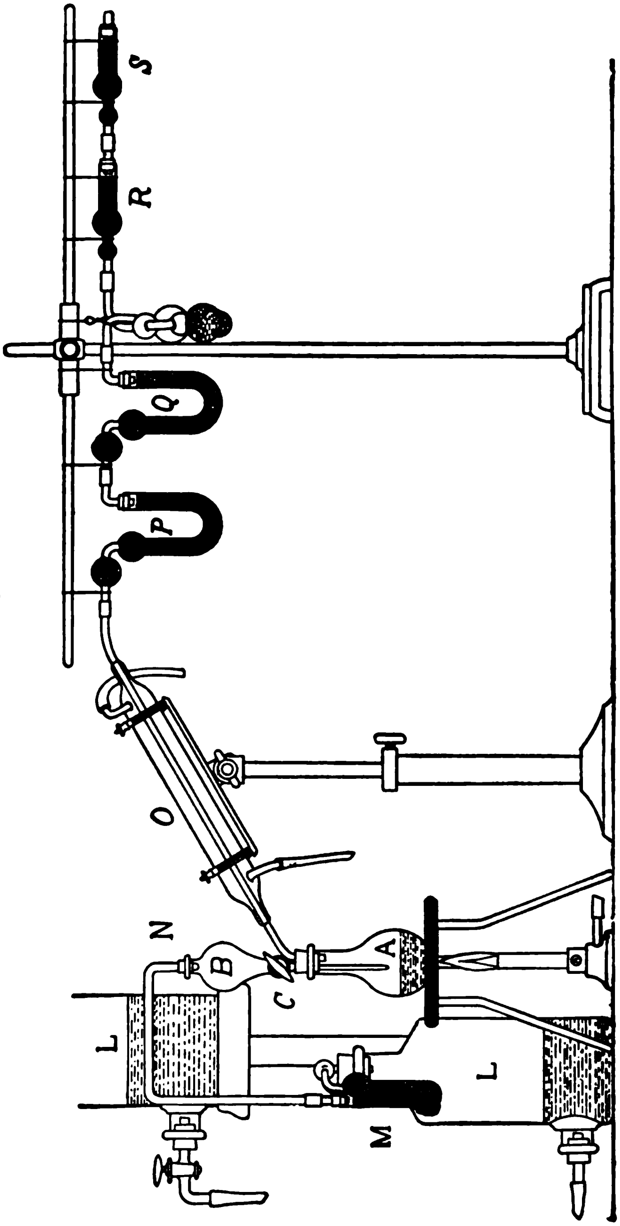
* J. L. Smith, Am. Jour. Sci. and Art, 1871, 3d Ser., i. (whole No. 101) 269.

FIG. 96.

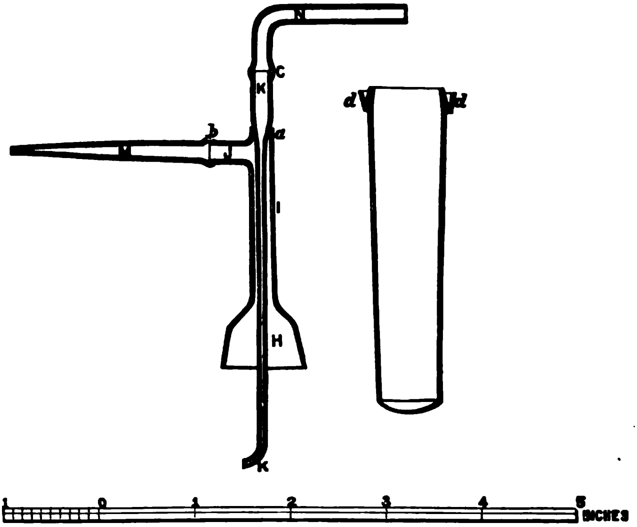


A. P contains anhydrous cupric sulphate, and Q contains calcium chloride. The potash-bulb and the drying-tube R form the absorption apparatus, and S is a safety-tube filled with calcium chloride to prevent R from absorbing moisture from the atmosphere. Weigh the absorption apparatus with the precautions mentioned on page 146, and connect the apparatus. Close the stopcock C, and draw a little air through the apparatus by means of a piece of rubber tubing attached to the end of S. Allow the tension of the air to draw the solution up into the rear limb of the potash-bulb, and if it remains there for a reasonable length of time the connections may be considered tight. Pour into the bulb B 10 c.c. hydrochloric acid diluted with about 65 c.c. water, connect the tube N, and by means of the stopcock C allow the acid to flow slowly into the flask A. When the acid has all run in, by opening slightly the stopcock in L, start a slow current of air through the apparatus. Warm the flask A, gradually increasing the heat until the solution boils, and continue the application of heat until a considerable amount of water has condensed in O. Allow it to cool while the current of air is continued, detach, and weigh the absorption apparatus. The increase of weight is the weight of carbonic acid.

DETERMINATION OF COMBINED WATER AND OF CARBON IN CARBONACEOUS MATTER.

The ores are very rare indeed in which the combined water can be determined accurately by simply heating them in a crucible and calling the loss by ignition "Water of Composition." Nor is the method of absorbing the moisture, driven off by heat, in a drying-tube much more reliable. The presence of pyrites, of organic matter, of graphite, and of manganese dioxide serves to complicate the problem. The water of composition may indeed be determined with great accuracy by heating the ore in a tube with lead chromate and potassium bichromate, exactly as described for the determination of carbon in iron and steel by direct combustion (page 129). The increase of weight of the U-tube which is attached to the end of the combustion-tube (and which in this case should be filled with granulated dried cupric sulphate) is the weight of "Combined Water" in the amount of ore used. By attaching the absorption apparatus we likewise obtain the total carbonic acid in the ore, or that existing as carbonic acid in the carbonates, and that due to the oxidation of any carbon existing as carbonaceous or organic matter or as graphite. By subtracting from the weight of carbonic acid thus obtained the amount of carbonic acid existing as carbonate and determined by the method last given, and multiplying the difference by .27273, we get the weight of "carbon in carbonaceous matter." When it is necessary to make a large number of these determinations, the matter is very much simplified by using the apparatus shown in Figs. 97 and 98.* Fig. 97 shows the details of a form of tubulated platinum crucible suggested by Dr. Gooch, which consists of the crucible with a flange at *d* into which fits the cap. This cap consists of a conical cover, H, drawn up vertically into the tube I. The horizontal tube J is burned into I, and through the centre of I passes the small tube K, which, expanding at *a*, is

FIG. 97.



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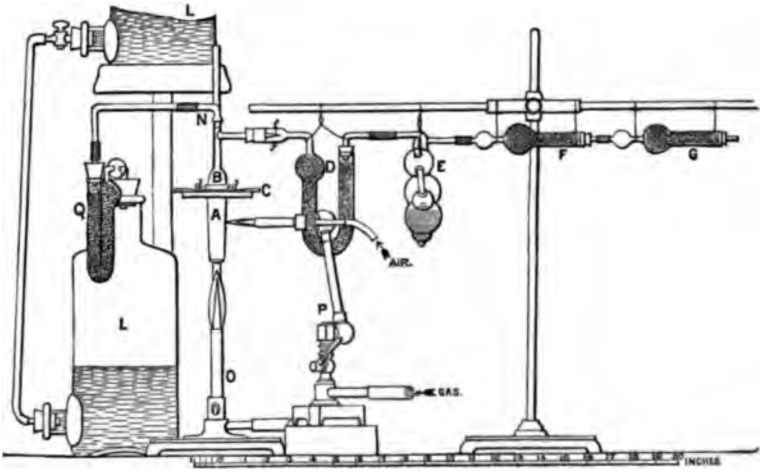
* Tenth Census of the United States, Mining Industries, xv. 519.

ned into I at this point, sealing it securely. The glass tubes N and M
fused to K and J at C and *b* respectively. In analyzing ores con-
ing much water or carbonic acid, use 1 gramme; for others, use 3
nmes. Weigh the finely ground ore, transfer it to a small agate
tar, and mix it thoroughly with from 7 to 10 grammes of previ-
ly fused potassium bichromate, transfer it to the crucible A (Fig. 98),
place it in an air-bath heated to 100° C. to drive off any hygro-
pic moisture. When perfectly dry, attach the cap B to the crucible,
stand the latter in the triangle C. Close the end N with a piece

FIG. 98.



ubber tubing in the other end of which is fitted a piece of glass rod.
ich the weighed drying-tube D, filled with calcium chloride, to the
zontal tube from B, by means of a thoroughly dried velvet cork.
ich the absorption apparatus E and F and the safety-tube G. Fill
outside of the flange *d* with small pieces of fused sodium tungstate,
with a blow-pipe flame, melt them, having previously immersed the
er end of A in a small beaker of ice-water. The expansion of the
n the crucible by the heat applied to melt the sodium tungstate will
e some bubbles through the potash-bulb E, and the subsequent cool-
of the air in A will cause the liquid in E to flow back into the

rear bulb. If the difference of level thus produced be maintained for some minutes, the connections may be considered tight. Connect N with the bottles L, as shown in the sketch, and start a current of air through the apparatus. The air is purified from carbonic acid and moisture by passing through Q, which is filled with fused caustic potash. Now, by means of the blast-lamp P, heat the crucible just above the top of the mixture, and gradually carry the heat downward, increasing it at the same time. This will keep the mixture from frothing and choking the tube. Finally, heat the bottom of the crucible by the burner O, and continue the application of the heat for ten minutes. During the whole of the operation the air passes through N and K into the crucible and out through J and M (Fig. 97) into D (Fig. 98), and so through the apparatus. The moisture from the ore should not be allowed to condense in the wide part of D at *f*, but should be driven forward into the calcium chloride by warming the tube at *f* with the flame of an alcohol lamp. Allow the apparatus to cool while the current of air is continued, then detach, and weigh the tube D and the absorption apparatus, and calculate the results as directed on page 256. When detached from the apparatus, the wide end of the tube D may be closed by a short cork, covered with tin-foil to prevent the absorption of moisture from the atmosphere. To clean the crucible, remove it from the stand, and, holding it in a piece of asbestos board in an inclined position, melt the sodium tungstate in the flange *d* with a blow-pipe flame and detach the cap. Dissolve out the bichromate by placing the crucible in a dish of hot water, clean out the ore, dissolve any adhering oxide in hydrochloric acid, wash the crucible and cap with hot water, dry them, and they will be ready for another determination.

DETERMINATION OF CHROMIUM.

The small amount of chromium which is found in some iron ores is generally converted into sodium chromate very readily by fusion with sodium carbonate and potassium nitrate. Fuse 1 or 2 grammes of the finely ground ore with ten times its weight of sodium carbonate and a little potassium nitrate. Treat the fused mass with water and wash it out into a small beaker. If the solution is colored by manganese, add a little alcohol, which will precipitate the manganese, leaving the solution, if chromium is present, slightly yellow. If the solution is colorless, it may be considered proof of the absence of chromium. Otherwise filter, wash the insoluble matter on the filter, dry it, grind it with ten times its weight of sodium carbonate and a little potassium nitrate, fuse, treat with water as before, filter, and add this filtrate to the other. Acidulate the combined filtrates with hydrochloric acid, evaporate to dryness to render the silica insoluble, and reduce the chromic acid to chromic oxide. Treat the mass with hydrochloric acid, dilute, filter, and precipitate the chromic oxide + alumina by ammonia. Boil for some minutes, filter, wash well with hot water, dry, and ignite the precipitate. Fuse with as little sodium carbonate and potassium nitrate as possible, treat with water, and wash the solution into a platinum dish. Evaporate the solution until it is very concentrated, adding from time to time crystals of ammonium nitrate to change all the carbonated and caustic alkali to nitrate. At each addition of ammonium nitrate the solution effervesces, and ammonium carbonate is given off. When the solution is nearly syrupy, the addition of ammonium nitrate no longer causes an effervescence, and the solution smells faintly of ammonia, add a few drops of ammonia, dilute, and filter. By this operation all the alumina, aluminum phosphate, manganese oxide, etc., are precipitated, and there remain in the solution only the alkalies and the alkaline chromate. To the filtrate add an excess of sulphurous acid in water, which instantly changes the color of the solution from yellow to green. Boil well, add an excess of ammonia, boil for a few minutes, filter on an ashless filter, wash well with hot water, dry, ignite, and weigh as chromic oxide.

Chrome iron ore is best decomposed by fusing .5 gramme of very finely ground ore with sodium peroxide as described in the analysis of ferro-chrome (page 208), and proceeding as there directed.

DETERMINATION OF TUNGSTEN.

Digest from 1 to 10 grammes of the ore in hydrochloric acid, adding nitric acid from time to time. When the ore appears to be perfectly decomposed, evaporate to dryness on the water-bath (a higher temperature is not admissible, as it may render the tungstic acid insoluble in ammonia), redissolve in hydrochloric acid, and evaporate again. Redissolve in hydrochloric acid, dilute, filter, wash with acidulated water, and finally with alcohol. Treat on the filter with ammonia, allowing the filtrate to run into a platinum dish, evaporate to small bulk, add excess of ammonia, filter, if necessary, into a platinum crucible, evaporate carefully to dryness, heat gently to drive off the ammonia, and ignite. Weigh as tungstic acid.

DETERMINATION OF VANADIUM.

Fuse 5 grammes of very finely ground ore with 30 grammes of sodium carbonate and from 1 to 5 grammes of sodium nitrate, and proceed exactly as in the determination of vanadium in pig-iron (page 197). A second fusion of the residue from the aqueous solution of the first fusion is hardly ever necessary.

DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity of iron ores is determined with much greater accuracy by employing the powdered material than by using lumps of the ore. The little flask shown in Fig. 99 was designed for this purpose by the late Mr. James Hogarth,* and its use avoids two difficulties experienced with the ordinary specific gravity bottle,—the expansion and overflow consequent upon transferring the flask at 60° F. to the higher temperature of the balance-case, and the necessity for waiting until the finely divided particles of the ore shall have settled before inserting the ɜr. These difficulties were overcome by melting a capillary tubulus : lower part of the neck of the flask, and by grinding in a stopper ʒ a small bulb above the capillary, to for expansion. The operation of deter- g the specific gravity of an ore is con- d as follows. Transfer a weighed amount ɜ ore to the flask, add enough water to it, and heat almost to the boiling-point ıcing the flask without the stopper in the ·bath. Place the flask under a bell-jar cted with an aspirator or air-pump, and all the air by allowing the water to boil me time at a reduced pressure. Remove ısk from the bell-jar, fill it to the tubulus cold water, insert the stopper, and cool ısk and its contents to about 60° F. By n on the stopper draw water through the ıs until it is slightly above the capillary : stopper, at which point a mark is scratched. When the flask and ntents are exactly at 60° F., adjust the volume exactly to the mark e capillary by touching a piece of blotting-paper to the end of the ıs or by drawing in a little water if the level is below the mark. he flask, allow it to acquire the temperature of the balance-case, and . Now, if W is the weight of ore taken, W′ the weight of the ıd water at 60° F., and K the weight of the flask and its contents : mark of water at 60° F., then

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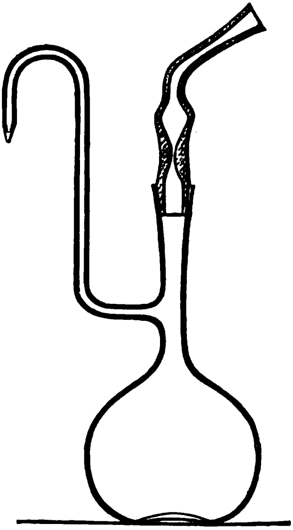
* Tenth Census of the United States, xv. 522.

FIG. 99.



$$\text{sp. gr.} = \frac{W}{W + K - W'}.$$

ɔtain K, fill the flask with boiled water, and treat it exactly as bed above.

METHODS FOR THE ANALYSIS

OF

LIMESTONE.

DETERMINATION OF INSOLUBLE SILICIOUS MATTER, ALUMINA AND FERRIC OXIDE, CALCIUM CARBONATE, AND MAGNESIUM CARBONATE.

WEIGH 1 gramme of the powdered limestone, previously dried at 100° C., place it in a No. 1 beaker, cover with a watch-glass, and pour in 5 c.c. of hydrochloric acid diluted with 25 c.c. of water and a little bromine-water. Digest on the hot plate until all the action ceases, wash the watch-glass with a fine jet of water, and evaporate to dryness. Redissolve in 10 c.c. hydrochloric acid diluted with 50 c.c. water, filter on a small ashless filter, wash well with hot water, dry, ignite, and weigh as "Insoluble Silicious Matter." Heat the filtrate to boiling, add a slight excess of ammonia, boil for a few minutes, filter, wash once or twice. Dissolve the precipitate on the filter in a little dilute hydrochloric acid, allowing the solution to run into the beaker in which the precipitation was made, wash well with water, dilute, boil, and reprecipitate by ammonia. Filter on a small ashless filter, allow this filtrate to run into the beaker containing the first one, wash well with hot water, dry, ignite, and weigh as alumina and ferric oxide. Heat the united filtrates to boiling, add enough ammonium oxalate to convert all the calcium and magnesium into oxalates.* Allow the precipitate of calcium oxalate to settle for fifteen or twenty minutes, filter on an ashless filter, wash with hot water, dry, ignite for some time over a Bunsen burner, and finally for fifteen minutes at the highest temperature of a blast-lamp. Cool in a desiccator, weigh quickly, ignite again over the blast-lamp for five minutes, cool, and weigh again. If this weight is the same, or nearly the same, as the previous one, call the amount lime. If the second weight is much less than the first, ignite, and weigh again until the weight is constant. The weight of lime, multiplied by 1.78459, gives the weight of calcium carbonate. Add to the filtrate from the calcium oxalate 30 c.c. of a saturated solution of microcosmic salt (sodium-ammonium phosphate), acidulate with hydrochloric acid, and evaporate the solution to about 300 c.c. If during the evaporation any precipitate should separate out, redissolve it in hydrochloric acid. Cool the evaporated solution in ice-water, and add ammonia drop by drop, stirring the solution, but being careful to avoid rubbing the sides of the beaker with the rod, as the precipitate of ammonium-magnesium orthophosphate is liable to adhere with great tenacity to those points or lines where the rod has touched the sides or bottom of the beaker. Continue the addition of ammonia until the solution is decidedly alkaline, and then add an amount equal to one-fourth of the neutralized solution. After the precipitate has begun to form, stir vigorously several times, allow to stand overnight, filter on an ashless filter, rub off with a "policeman" any of the precipitate that may adhere to the beaker, wash with a mixture of 1 part ammonia and 2 parts water, containing 100 grammes of ammonium nitrate to the litre, dry, ignite with great care, as directed on page 238, cool, and weigh as magnesium pyrophosphate, which, multiplied by .36212, gives the weight of magnesia, and, multiplied by .75760, gives the weight of magnesium carbonate.

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* 25 c.c. of the saturated solution is about the proper quantity.

Limestones, besides the ordinary constituents mentioned above, may contain small amounts of phosphoric acid, sulphur as sulphate or as pyrites, titanic acid, organic matter, combined water, alkalies, manganese, fluorine, and in rare instances nearly all the metals found in iron ores. For most of these the methods described in the analysis of iron ores may be employed. Very often the amounts of silica and alumina are required in calculating mixtures for the blast-furnace, and, as the matter insoluble in hydrochloric acid consists usually of alumina, lime, and magnesia silicates, it would be necessary in accurate work to decompose the "Insoluble Silicious Matter" by fusion with sodium carbonate and to make a separate analysis of it, as described on page 237. It is, indeed, much better to make the analysis in this way than to add the filtrate from the silica to the main solution, for the calcium oxalate is sure to carry down some of the sodium salts with it and thus very materially complicate the analysis.

After weighing the alumina and ferric oxide from the "Insoluble Silicious Matter" and that from the portion soluble in dilute hydrochloric acid to determine the ferric oxide, fuse the two precipitates with a little sodium carbonate, dissolve in water, transfer to a beaker and acidulate with hydrochloric acid, add a few small crystals of citric acid to the clear solution, then excess of ammonia and ammonium sulphide. Allow the precipitate of ferrous sulphide to settle, filter, wash slightly, dissolve in hydrochloric acid, add a little bromine-water, boil the solution, precipitate by ammonia, filter, wash, ignite, and weigh as ferric oxide. The weight of ferric oxide subtracted from the weight of the total alumina + ferric oxide gives, of course, the weight of alumina.

The lime and magnesia in the "Insoluble Silicious Matter" should not be calculated as carbonates, but should be considered as existing as lime and magnesia.

To determine phosphoric acid in limestones, treat 20 grammes with dilute hydrochloric acid, filter from the insoluble silicious matter, to the filtrate add a few drops of ferric chloride solution, then ammonia until the solution is alkaline to litmus-paper,* and acetic acid to decided acid reaction. Boil for a few minutes, filter, wash once with hot water, dissolve in hydrochloric acid on the filter, allowing the solution to run into the beaker in which the precipitation was made, add the solution from the treatment of the insoluble silicious matter mentioned below, dilute, and reprecipitate exactly as before with ammonia and acetic acid.

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* If the precipitate is not decidedly red in color, acidulate with hydrochloric acid and add more ferric chloride solution.

Dissolve this precipitate on the filter in dilute hydrochloric acid, allowing the solution to run into a No. 1 beaker, wash the filter with hot water, evaporate the solution down almost to dryness, and precipitate the phosphoric acid as directed on page 80 *et seq.*

Ignite the insoluble silicious matter with hydrofluoric acid and a few drops of sulphuric acid, evaporate until fumes of sulphuric anhydride are given off, fuse with sodium carbonate, digest in water, filter, acidulate the solution with hydrochloric acid, and add it to the solution of the first precipitate in the soluble portion as mentioned above.

Instead of treating the insoluble silicious matter with hydrofluoric and sulphuric acids, it may be fused at once with sodium carbonate, the fused mass treated with water, filtered, the filtrate acidulated, evaporated to dryness, redissolved in water slightly acidulated with hydrochloric acid, filtered, and the filtrate added to the solution of the first precipitate by ammonia and acetic acid as above.

To determine sulphur in limestone, fuse 1 gramme with sodium carbonate and potassium nitrate exactly as in the determination of sulphur in iron ores (page 225 *et seq.*).

To determine sulphates, proceed as in the analysis of iron ores for these substances (page 226).

METHODS FOR THE ANALYSIS

OF

CLAY.

CLAY is essentially silica, mixed with aluminum, calcium, magnesium, potassium, and sodium silicates. These silicates are hydrated, so that clay usually contains from 6 to 12 per cent. of water of composition. Besides these usual constituents, clay may contain ferric oxide, titanic acid, pyrites, organic matter, phosphoric acid, and occasionally some of the rarer elements, such as vanadium.

Clay being practically unacted on by hydrochloric acid, it is necessary to proceed as follows. Fuse 1 gramme of the finely ground clay, dried at 100° C., with 10 grammes of sodium carbonate and a very little sodium nitrate. Run the fused mass well up on the sides of the crucible, allow it to cool, and treat it with hot water until thoroughly disintegrated, transferring the liquid from time to time to a platinum dish. Treat the crucible with hydrochloric acid, add this to the liquid in the dish, acidulate with hydrochloric acid, and evaporate to dryness in the air-bath. Treat the mass with water and a little hydrochloric acid, evaporate again to dryness, and treat with 15 c.c. hydrochloric acid and 45 c.c. water. Allow it to stand in a warm place for fifteen or twenty minutes, add 50 c.c. water, and filter on an ashless filter. Wash thoroughly with hot water acidulated with a few drops of hydrochloric acid, dry, ignite, heat for three or four minutes over the blast-lamp, and weigh. Treat the precipitate with hydrofluoric acid and a few drops of sulphuric acid, evaporate to dryness, ignite, and weigh. The difference between the two weights is silica. If any appreciable residue remains in the crucible, treat it with a little hydrochloric acid, and wash it out into the filtrate from the silica. Transfer the filtrate from the silica to a large platinum dish, heat it to boiling, add an excess of ammonia, boil until the smell of ammonia is quite faint, filter on an ashless filter, and wash several times with hot water. Stand the filtrate and washings aside, and treat the precipitate on the filter with a mixture of 15 c.c. hydrochloric acid and 15 c.c. water (cold). Allow the solution to run into a small clean beaker, replace this by the platinum dish in which the precipitation was made, pour the solution on the filter again, and repeat this operation until the precipitate has completely dissolved. Rinse the beaker and wash the filter thoroughly with cold water, dry, and preserve it. Reprecipitate by ammonia, as above directed, filter on an ashless filter, wipe the dish with small pieces of filter-paper, add these to the precipitate, and wash thoroughly with hot water. Dry, ignite the precipitate and filter, and the filter from the first precipitation, heat for a few minutes over the blast-lamp, cool, and weigh as alumina and ferric oxide. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with water, wash it into a small beaker, allow the residue to settle, decant off the clear, supernatant fluid, treat the residue with hydrochloric acid, and determine the iron volumetrically, or add citric acid and ammonia, and after precipitating the iron as sulphide, filter, wash, dissolve in hydrochloric acid, oxidize with bromine-water, and precipitate the ferric oxide by ammonia. Filter, wash, dry, ignite, and weigh as ferric oxide. Subtract the weight of ferric oxide from the alumina + ferric oxide found above, and the difference is alumina.

As the amounts of calcium and magnesium in clay are very small, the filtrate and washings from the second precipitation of alumina + ferric oxide may be rejected and the lime and magnesia determined in the first filtrate as directed on page 263.

To determine the alkalies in clay, treat 2 grammes of the finely ground material in a platinum dish with 4 c.c. of strong sulphuric acid and 40 or 50 c.c. of redistilled hydrofluoric acid. Stir it from time to time with a platinum wire or rod, heating carefully, until the clay is entirely decomposed and no more gritty substance can be felt under the rod. Evaporate to dryness, and heat until no more fumes of sulphuric anhydride are given off. The entire operation should be carried on under a hood with a good draft, as hydrofluoric acid is poisonous, and the evaporation may safely be conducted on the little arrangement shown in Fig. 10, page 20. Allow the dish to cool, add about 50 c.c. water and a little hydrochloric acid, and heat until the mass is all dissolved. If any of the clay has escaped decomposition, filter into another platinum dish, wash the insoluble matter on the filter, dry, ignite, and decompose it in the crucible with hydrofluoric and sulphuric acids. Dissolve the mass in the crucible after evaporating off the hydrofluoric and sulphuric acids, and add the solution to the main solution in the dish. Dilute this solution to 300 or 400 c.c. with hot water, heat to boiling, add an excess of barium hydrate, boil for a few minutes, and filter. Allow the precipitate to drain well on the filter, remove the filtrate, which should be in a platinum dish, to a light, and evaporate it down. Pierce the filter with a wire or rod, and wash the precipitate into the dish in which the precipitation was made with a jet of hot water. Dilute to 300 or 400 c.c., heat to boiling, filter, and wash several times with hot water. Add this filtrate to the first one, evaporate to dryness, and proceed exactly as directed for the determination of alkalies in the "Insoluble Silicious Matter" from iron ores (page 252).

Instead of decomposing the clay with hydrofluoric and sulphuric acids, the method given by J. Lawrence Smith may be used for determining alkalies. Place 1 gramme of the finely ground clay in a porcelain or agate mortar, add an equal weight of granular ammonium chloride,* and grind the two together to mix them. Add 8 grammes of calcium carbonate,† and grind the entire mass so as to obtain an intimate mixture of the whole. Transfer to a capacious platinum crucible, cover with a close-fitting lid, and heat carefully to decompose the ammonium chloride, which is accomplished in a few minutes. Heat gradually to redness, and keep the bottom of the crucible at a bright red for about an hour. Allow the crucible to cool, and if the mass is easily detached from the crucible, transfer it to a platinum ish and add about 80 c.c. of water. Wash the crucible and lid with oiling water, pouring washings into the dish. Heat the water in the dish o boiling, and, when the mass has completely slaked, filter into another latinum dish and wash the mass on the filter with hot water. If the emi-fused mass in the crucible is not easily detached, place the crucible n its side in the dish, add about 100 c.c. water, and heat until the mass isintegrates. Remove the crucible, rinse it, and filter as above directed. o the filtrate add about 1½ grammes of pure ammonium carbonate, vaporate on the water-bath, or very carefully over a light, until the olume of the solution is reduced to about 40 c.c., add a little more mmonium carbonate and a few drops of ammonia, and filter on a mall filter. Evaporate the filtrate carefully after adding a few drops ore of ammonium carbonate to make certain that all the lime has een precipitated. If any further precipitate appears, filter into a latinum crucible and evaporate to dryness. Heat carefully to dull edness to drive off any ammonium salts, and weigh the residue as otassium-sodium chloride. Separate the potash and soda as directed n page 252.

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* See page 45.

† See page 52.

Determine the water of composition by igniting 1 gramme of the clay r twenty minutes at a bright red heat, when the loss of weight will represent the water. In the presence of much organic matter or pyrites the ethod given for the determination of water of composition in iron ores page 255) may be used.

To determine titanic acid, treat 2 grammes of the finely ground clay in large platinum crucible with hydrofluoric acid and 5 c.c. sulphuric acid. vaporate off the hydrofluoric acid and heat carefully until the greater part f the sulphuric acid is volatilized. Allow the crucible to cool, add 10 rammes of sodium carbonate, and fuse for thirty minutes at the highest emperature obtainable by a Bunsen burner. Run the fused mass well up n the sides of the crucible, and allow it to cool. Treat the fused mass ith water, transfer it to a beaker, and filter. Wash the insoluble matter lightly on the filter, dry, ignite, and fuse it again with sodium carbonate. issolve in water as before, and filter. By this method of treatment nearly ll of the alumina will be dissolved and separated from the titanic acid.

Fuse the insoluble matter left on the filter with sodium carbonate, and determine the titanic acid as directed on page 229.

When alkalies are determined, the precipitated alumina may be used for the determination of titanic acid. In this case dry the precipitate of alumina, etc., separate it from the filter, ignite the two filters, add the ash to the dried (not ignited) precipitate of alumina, etc., and fuse with sodium carbonate as above.

METHODS FOR THE ANALYSIS

OF

SLAGS.

BLAST-FURNACE slags contain silica, alumina, lime, magnesia, and alka- s always, generally also ferrous oxide, manganous oxide, and sulphur, d occasionally titanic acid, small amounts of phosphoric acid, and such etallic oxides as may exist in the ores, fluxes, or fuel used in the furnace. lphur, which is occasionally present in considerable amounts, is consid- ed to exist in the slag as calcium sulphide.

The method used for the determination of the principal ingredients pends upon whether the slag is capable of being entirely or but partially composed by hydrochloric acid.

In the first case weigh 1 gramme of the finely ground slag, place it in a atinum or porcelain dish, add 20 c.c. of water, and shake the dish until e material is thoroughly disseminated through the water. Add gradually c.c. hydrochloric acid, with constant stirring, and finally heat the dish refully. The slag will dissolve completely to a clear liquid, but, after ating for a short time, will suddenly form a solid jelly. Evaporate care- lly to dryness, treat with a few c.c. of dilute hydrochloric acid and a little omine-water, evaporate again to dryness, and add 15 c.c. hydrochloric id and 45 c.c. water. Allow to stand fifteen or twenty minutes in a warm ace, add 50 c.c. water, filter on an ashless filter, wash thoroughly with hot ater, dry, ignite, and weigh. Treat the material in the crucible with a tle water, add 2 or 3 drops sulphuric acid and enough hydrofluoric acid dissolve it. Evaporate to dryness, ignite, and weigh. The loss of eight is silica.

Any residue in the crucible after the volatilization of the silica is to be added to the alumina ferric oxide. Heat the filtrate obtained above, diluted to 500 c.c., to boiling, add a slight excess of ammonia, boil for a few minutes, filter on an ashless filter, and wash two or three times with boiling water. Stand the filtrate aside, and pour on the precipitate in the filter a mixture of 15 c.c. hydrochloric acid and 30 c.c. cold water, allowing the solution to run into the dish in which the precipitation was made. Alumina precipitated in this way seems generally to dissolve more readily in cold than in hot dilute hydrochloric acid, but it is often necessary to break up the precipitate on the filter with a rod, and pour the acid solution back on the filter several times after it has run through, or sometimes to pierce the filter with a rod or wire and wash the precipitate still undissolved into the dish. Wash the filter well with water, dry it, and keep it to ignite with the alumina, etc. Heat the filtrate and washings to boiling, reprecipitate by ammonia, filter on an ashless filter, clean off any adhering precipitate from the dish with filter-paper, add it to the precipitate on the filter, wash well with hot water, dry, ignite, after adding the filter on which the first precipitation was filtered, and weigh as alumina, etc. Add to this the weight of the residue from the treatment of the silica by sulphuric and hydrofluoric acids,* and the sum is the total alumina + ferric oxide + phosphoric acid + titanic acid.

Evaporate the two filtrates obtained above down to about 300 c.c., transfer to a No. 3 beaker, add a few drops of ammonia and enough ammonium sulphide to precipitate the manganese. Filter off and determine the manganese as directed on page 232, in the "Analysis of Iron Ores." To the filtrate from the manganese sulphide add a slight excess of hydrochloric acid, boil until all the hydrogen sulphide is driven off, filter from any precipitated sulphur, and determine the lime and magnesia as directed on page 263 *et seq.*, in the "Analysis of Limestone."

To determine the ferrous oxide, fuse the ignited precipitate of alumina, etc., obtained above, with 5 grammes of sodium carbonate, at a very high temperature, for at least thirty minutes. Allow the crucible to cool, treat the fused mass with water, transfer to a beaker, allow the insoluble matter to settle, decant the clear, supernatant liquid through a filter, and treat the residue with hydrochloric acid. Pour the solution through the filter to take up any iron that may have been suspended in the liquid decanted through it, and determine the iron volumetrically or by precipitation as sulphide in the solution to which citric acid and an excess of ammonia have been added, as on page 245. When the slag contains no appreciable amount of manganese, the precipitation by ammonium sulphide (page 272) may be omitted and the lime precipitated at once from the concentrated solution.

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* This residue should be examined for lime.

For the analysis of slags that are not entirely decomposed by hydrochloric acid, recourse must be had to fusion with sodium carbonate and a little sodium nitrate, exactly as described for the analysis of clay (page 266 *et seq.*). After filtering off the silica as directed (page 266), proceed with the analysis as described for slags decomposed by hydrochloric acid (page 271 *et seq.*). As, however, the calcium oxalate is very liable to carry down sodium salts with it, it is always well, after igniting the calcium oxalate, to dissolve it in dilute hydrochloric acid, transfer the solution to a platinum dish, dilute to 300 c.c. with hot water, add an excess of ammonia, and precipitate boiling by 30 c.c. of a saturated solution of ammonium oxalate. Filter, wash, ignite, and weigh in the usual manner.

For the determination of sulphur in slags, fuse 1 gramme with sodium carbonate and a little potassium nitrate, and proceed exactly as directed for the determination of sulphur in iron ores (page 225 *et seq.*). Calculate the total sulphur as calcium sulphide and the remainder of the calcium as lime.

For the determination of alkalies, titanic acid, etc., proceed as directed for the determination of these substances in clay.

Converter slags, open-hearth slags, refinery slag, tap cinder, mill cinder, etc., are analyzed by the methods described for the analysis of iron ores. In the case of slags obtained from the manufacture of steel by the basic process, which usually contain very large amounts of phosphoric acid, proceed as follows. Treat 1 gramme of the finely ground slag in a small beaker with 15 c.c. hydrochloric acid and a little nitric acid until it is decomposed. Evaporate to dryness, redissolve in 10 c.c. hydrochloric acid and 20 c.c. water, dilute, filter, and weigh the silica. To the filtrate diluted to 500 c.c. add a solution of ferric chloride and a slight excess of ammonia, if the precipitate is not decidedly red in color, acidulate carefully with hydrochloric acid, add more ferric chloride solution, and then a slight excess of ammonia. Add acetic acid to slight acid reaction, heat to boiling, filter and wash slightly with boiling water, stand the filtrate aside, and dissolve the precipitate on the filter in hydrochloric acid, allow the solution to run into the beaker in which the precipitation was made, wash the filter thoroughly with cold water, dilute the filtrate to about 400 c.c., add a slight excess of ammonia and then acetic acid, boil, and filter as before. Add this filtrate to the first, evaporate down, and determine the manganese, lime, and magnesia, as directed in the case of blast-furnace slags (page 272). Dissolve the precipitate on the filter in hydrochloric acid, dissolving any iron that may adhere to the beaker in a few drops of the same acid, pour it on the filter, and wash the beaker and filter well with water. Allow the solution and washings to run into a No. 3 beaker, and add about 10 grammes of citric acid and an excess of ammonia. To this solution, which should be cold, and should measure about 300 c.c., add, drop by drop, 50 c.c. of magnesia-mixture, stirring carefully, without touching the sides of the beaker with the rod. Add about one-third the volume of the solution of ammonia, allow the beaker to stand in ice-water for some time, stir vigorously several times, and after a few hours filter (preferably on a Gooch crucible), wash with ammonia-water of the usual strength, ignite carefully, and weigh as magnesium pyrophosphate. Any alumina in the slag will be in the filtrate from the ammonium-magnesium phosphate, and may be determined by the method on page 245. Determine the iron volumetrically in a separate portion, and calculate to ferrous oxide. Determine any other elements present by the methods under "Analysis of Iron Ores."

Phosphoric acid cannot well be determined in basic slags by fusion with sodium carbonate, as calcium phosphate is not readily decomposed by this method, and its employment may lead to error.

METHOD FOR THE ANALYSIS

OF

FIRE-SANDS.

As sand contains comparatively very small amounts of alumina, lime, and magnesia, and a very large amount of silica, it is best to proceed with the analysis as follows. Place 2 grammes of the finely ground sand in a large platinum crucible, moisten it with cold water, add 6 or 8 drops of sulphuric acid, and then gradually enough hydrofluoric acid to dissolve it. Evaporate to dryness (under a hood, of course), and heat to redness to drive off the sulphuric acid. Allow the crucible to cool, add a little sodium carbonate, and fuse. Dissolve the fusion, when cold, in water, add an excess of hydrochloric acid, evaporate to dryness, redissolve in hydrochloric acid and water, filter from silica, and determine the alumina, lime, and magnesia as usual. Ignite 1 gramme of the sand and determine the loss, which will be water and organic matter (if present).

It is well to note that in the presence of alumina it is almost impossible to drive off all the silica by treatment with hydrofluoric and sulphuric acids, and the small amount of silica remaining after this treatment must be separated as directed above.

Add together the percentages of water, alumina, lime, and magnesia, subtract the sum from 100, and call the remainder silica.

METHODS FOR THE ANALYSIS

OF

COAL AND COKE.

A PROXIMATE analysis affords a very rapid and comparatively simple way of classifying and valuing coal. From the nature of the material, the determinations cannot be absolute, but inferences may be drawn from the relative proportions of Moisture, Volatile Combustible Matter, and Ash. Therefore it is essential that the analysis should be performed in such a way as to obtain the most concordant results.

PROXIMATE ANALYSIS.*

Determination of Moisture.

" Dry one gramme of the coal in an open porcelain or platinum crucible at from 104° to 107° C. for one hour, best in a double-walled bath containing pure toluene.† Cool in a desiccator and weigh covered.

" With coals high in moisture, and in all cases where accuracy is desired, determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter. Thus, if 1 per cent.

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* From the Report of the Committee on Coal Analysis to the American Chemical Society, Journal of the American Chem. Soc., xxi. 1116. William A. Noyes, W. F. Hillebrand, and C. B. Dudley, committee.

† Victor Meyer, Ber. d. Chem. Ges., 17, 2999.

more of moisture is found in the coarsely ground sample, a total of 1 per cent. must be subtracted from the quantities of the other constituents as determined with the powdered sample. Or, in the form of a rule: divide the difference in moisture by the per cent. of other constituents than moisture as found in the powdered coal by the quotient and subtract the resulting product from the amount of the given constituent.

"Thus, suppose the results of an analysis give:

	Coarsely ground Coal.	Powdered Coal.
Moisture	12.07	10.39
Volatile combustible matter		34.25,

then the correction factor will be

$$\frac{12.07 - 10.39}{100 - 10.39} = \frac{1.68}{89.61} = 0.0187,$$

and the true per cent. of volatile combustible matter will be

$$34.25 - (34.25 \times 0.0187) = 33.61.$$

"It is possible that volatile combustible matter and ash may be determined with the coarsely ground coal without serious error, but we have not enough data at our command to warrant such a recommendation.

"The toluene bath is recommended for convenience, but any other bath at the proper temperature will answer equally well. In all cases recorded below the coals gained in weight, probably from oxidation, after one hour's heating, so that longer heating is not only unnecessary but undesirable. A higher temperature appears also to be undesirable."

Determination of Volatile Combustible Matter.

"Place 1 gramme of fresh, undried, powdered coal in a platinum crucible weighing 20 or 30 grammes and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom from 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find

Volatile Combustible Matter, subtract the per cent. of moisture from the loss found here." (The weight of the material left in the crucible is "coke.")

Determination of Ash.

"Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

"When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash; and, since three atoms of oxygen replace four atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee does not recommend such a correction for 'proximate' analyses. When analyses are to be used as a basis for calculating the heating effect of the coal a correction should be made."

Determination of Fixed Carbon.

"This is found by subtracting the per cent. of ash from the per cent. of coke as found above. Sulphur, which passes partly into the Volatile Combustible Matter and partly into the coke, is not considered in the calculation."

Determination of Sulphur.

Weigh 1 gramme of the finely ground coal or coke, and mix it thoroughly, by grinding in a large agate or porcelain mortar, with 10 grammes of dry sodium carbonate and 6 grammes of potassium nitrate. During the mixing it is well to have the mortar on a large sheet of white glazed paper, to catch any particles that may be thrown from it. Transfer the mixture to a large platinum crucible, clean the mortar by grinding a little sodium carbonate in it, transfer this and any particles that may be on the paper to the crucible, cover the latter with a lid, and place it on a triangle over an alcohol lamp. Heat the crucible very carefully, and raise the heat very slowly, cautiously removing the lid of the crucible from time to time to see that the fusion does not boil over. It is very necessary that an alcohol lamp be used for this fusion, as the sulphur in ordinary gas will certainly vitiate the result. When the mass in the crucible is in a tranquil state of fusion, run it up on the sides of the crucible, cool, treat with hot water, and wash out into a small clean beaker. Filter from the insoluble matter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Redissolve in water with a few drops of hydrochloric acid, filter, dilute the filtrate to about 500 c.c., heat to boiling, and add from 10 to 20 c.c. of a strong solution of barium chloride.* Allow the precipitated barium sulphate to settle, decant the clear, supernatant fluid through a filter or a felt on a Gooch crucible, heat the precipitate with a solution of ammonium acetate,† transfer it to the filter, wash well with hot water, dry, ignite, and weigh as barium sulphate, which, multiplied by .13756, gives the weight of sulphur. The time of the operation may often be very much shortened by adding an excess of ammonia to the acidulated filtrate of the aqueous solution of the fusion, and boiling the solution while passing a rapid current of carbonic acid gas through it. This precipitates the silica, alumina, etc., and, after filtering this off, acidulate by hydrochloric acid, and precipitate the barium sulphate as above directed.

A blank determination, using the same amount of sodium carbonate, potassium nitrate, and hydrochloric acid, should always be made with every new lot of reagents, and the amount of barium sulphate found subtracted from the amount of barium sulphate in every analysis before calculating the amount of sulphur in the coal or coke.

Determination of Sulphur.‡ (Eschka's Method.)

"Eschka's method is recommended for general use. The following directions, which are given for the convenience of those using this report, are those of G. L. Heath § with slight modifications.

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* See page 51. † See page 45.

‡ From Report of Com. on Coal Analysis, *ante*.

§ Journal American Chem. Soc., xx. 630.

"Mix thoroughly 1 gramme of the finely powdered coal* with 1 gramme of magnesium oxide and ½ gramme of dry sodium carbonate in a thin platinum dish having a capacity of from 75 to 100 c.c. A crucible may be used, but a dish is preferred. The magnesium oxide should be light and porous, not a compact, heavy variety.

"The dish is heated on a triangle over an alcohol lamp, held in the hand at first. *Gas must not be used*, because of the sulphur it contains. The mixture is frequently stirred with a platinum wire and the heat raised very slowly, especially with soft coals. The flame is kept in motion and barely touching the dish, at first, till strong glowing has ceased, and is then increased gradually till, in fifteen minutes, the bottom of the dish is at a low red heat. When the carbon is burned, transfer the mass to a beaker and rinse the dish, using about 50 c.c. of water. Add 15 c.c. of saturated bromine-water and boil for five minutes. Allow to settle, decant through a filter, boil a second and third time with 30 c.c. of water, and wash till the filtrate gives only a slight opalescence with silver nitrate and nitric acid. The volume of the filtrate should be about 200 c.c. Add 1½ c.c. of concentrated hydrochloric acid or a corresponding amount of dilute acid (8 c.c. of an acid of 8 per cent.). Boil till the bromine is expelled, and add to the hot solution drop by drop, especially at first, and with constant stirring, 10 c.c. of a 10 per cent. solution of barium chloride. Digest on the water-bath or over a low flame, with occasional stirring till the precipitate settles clear quickly. Filter and wash, using either a Gooch crucible or a paper filter. The latter may be ignited moist in a platinum crucible, using a low flame till the carbon is burned.

"In the case of coals containing much pyrites or calcium sulphate, the residue of magnesium oxide should be dissolved in hydrochloric acid and the solution tested for sulphuric acid.

"If desirable, the burning of the coal with Eschka's mixture may be carried out in a muffle, from twenty to thirty minutes being required."†

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*With coals high in moisture a correction may be necessary on account of the loss of water in powdering the coal. (See above under Moisture.)

† Rothe, Stahl und Eisen, xii. 31 (1894).

In reporting the results of a coal analysis the sulphur should always be reported as a separate matter, and no attempt should be made to distribute it between the Volatile Combustible Matter, Fixed Carbon, and Ash. The reason for this is obvious when we consider the conditions in which sulphur exists in coal, and the difficulty which attends any attempt to determine the amount existing in any one condition.

Sulphur is known to exist in coal in three conditions,—as a metallic sulphide, such as pyrites, as calcium or barium sulphate, and as a sulphuretted hydrocarbon. In a proximate analysis of coal about one-half the sulphur in any pyrites present and all the sulphur existing as a sulphuretted hydrocarbon are probably driven off with the Volatile Combustible Matter. The rest of the sulphur from the pyrites is oxidized and driven off during the burning of the Fixed Carbon (iron sulphate being easily decomposed at a bright red heat) unless the sulphuric acid formed is taken up by an alkali or alkaline earth.

The nearest approach we can make to a determination of the conditions in which the sulphur exists in any coal is to make a determination of the total sulphur by fusion, and a determination of the sulphuric acid in the ash. By subtracting the sulphur found by the latter determination from the total sulphur the difference may be taken to represent the amount existing as sulphur (in the form of sulphide), and the amount found in the ash as that existing as sulphuric anhydride (in the form of sulphate). These results will be correct if the coal contains no carbonates of the alkalies or alkaline earths.

Determination of Phosphoric Acid.

Burn off 10 grammes of the coal or coke in a crucible, or, as in anthracite coal or coke this is a very tedious operation, burn it off in a large platinum boat in a tube in a current of oxygen. A boat 4 inches (102 mm.) long, and wide enough to fit in a tube ¾ of an inch (19 mm.) in diameter, will hold 10 grammes very easily, and by its use this amount of coke or anthracite coal may be burned off in a current of oxygen in about one and a half hours. Treat the ash with hydrochloric acid to dissolve any calcium phosphate, filter, and wash well with water. Stand the filtrate aside, dry, ignite, and fuse the insoluble matter with sodium carbonate. Dissolve in water, filter from the insoluble matter, acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Redissolve in water and a little hydrochloric acid, add this filtrate to the hydrochloric acid filtrate from the first treatment of the ash, add a little ferric chloride solution and a slight excess of ammonia. Acidulate with acetic acid, heat to boiling, boil for a few minutes, filter, and wash the precipitate once or twice with boiling water. Dissolve the precipitate in hydrochloric acid, evaporate nearly to dryness, add citric acid, magnesia-mixture, and ammonia, and precipitate as directed on page 84. Filter, ignite, and weigh the magnesium pyrophosphate as there directed. Or, after dissolving the acetate precipitate, as above, in hydrochloric acid, evaporate down, and precipitate the phosphoric acid by molybdate solution, as directed on page 97 *et seq.*

ULTIMATE ANALYSIS.*

"It seems to be unnecessary to give directions for the determinations of carbon, hydrogen, and nitrogen here. In determining carbon and hydrogen, lead chromate or some other means for retaining sulphur must, of course, be used. The amount of nitrogen is so small that the use of a copper spiral is not necessary."

"The method to be used in calculating the oxygen of the coal presents, perhaps, the question of greatest difficulty. If we could be sure that all of the sulphur is present in the form of pyrites, and that this is converted into ferric oxide in the ash, the oxygen should be found by subtracting from 100 the sum of carbon, hydrogen, nitrogen, ash, and five-eighths of the sulphur. This is probably the safest rule which can be given for general use, and especially for coals high in sulphur. The operator should, however, satisfy himself as to whether the ash is practically free from sulphates, and, if possible, whether the sulphur is mainly in the form of pyrites. If necessary, the rule should be modified, in particular cases, accordingly."

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* From Report of Com. on Coal Analysis, *ante.*

Heating Effect.

"In the preliminary report the recommendation was made that the heating effect be given on the basis of the coal burned to vapor of water at 100° C. After some criticism from others and further consideration, we have concluded to recommend that results be given for the coal burned to liquid water at the ordinary temperature. The reasons for this recommendation are that this appears to be the common practice in this country, and because coals are burned to liquid water in the bomb calorimeter, which undoubtedly furnishes the best determinations of heating effect at present available. Engineers and others will, of course, understand that the heating effect, when stated in this manner, includes from 3½ to 4 per cent. of heat which can never be secured under the conditions of practical use.

"The most reliable formula for the calculation of the heating effect of a coal burned to liquid water is that of Dulong, which gives the calorific power in calories per kilogramme.

$$\text{"Calorific power} = 8080\ C + 34{,}460\ (H - \frac{1}{8}\ O) + 2250\ S.$$

"For the calculation of the oxygen, see the paragraph above on ultimate analysis."

"The calorific power in British Thermal Units per pound may be found by multiplying that in calories per kilogramme by nine-fifths."

"The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogramme by 536, or the number of British Thermal Units per pound by 965, and subtracting from the result one-seventh more than the amount of water formed by burning one kilogramme of the coal. The addition of one-seventh is given because the liquid water, on the basis of which the heating effect is given, must be considered as changed from water at ordinary temperature to steam at 100° C. The amount to be subtracted may be taken as 0.55 for most bituminous coals. The result gives the theoretical number of kilogrammes, or pounds, of water converted into steam from, and at, 100° C. by one kilogramme, or pound, of coal."

"The rule given, tentatively, in our preliminary report for the calculation of heating effect, from the amount of combustible matter present in bituminous coals, has been found to be of limited application."

METHODS FOR THE ANALYSIS

OF

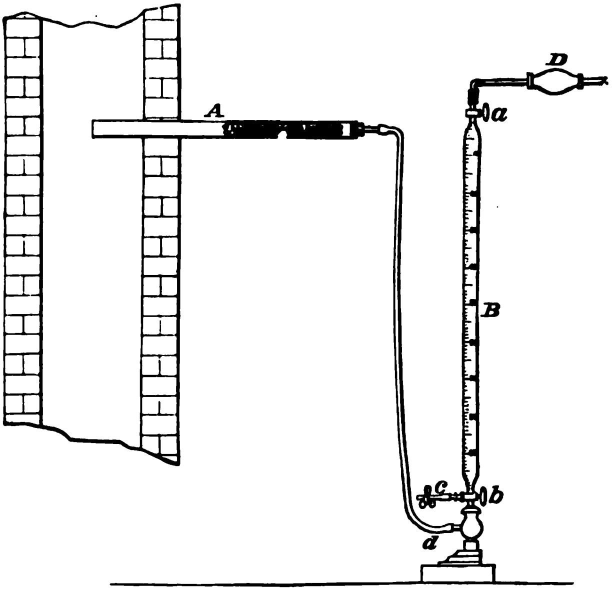
GASES.

THE technical analysis of gases is of growing importance, and a knowledge of the methods of analysis and of the manipulation involved is now generally necessary to the iron chemist. For ease of manipulation, and for the accuracy of the results obtained by its use, Hempel's form of apparatus is generally to be preferred. It consists essentially of a burette for holding and measuring the gas, B, Fig. 100 (the modified Winkler's gas-burette), and a pipette, G (Fig. 103), which holds the reagent. By means of the level-tube A, filled with water, the gas is forced into the pipette, where it is brought in contact with the reagent and afterwards returned to the burette and measured. By the use of a series of these pipettes, each filled with a separate reagent, the various constituents of the gas under examination are absorbed and their volumes estimated.

COLLECTING SAMPLES.

Fig. 100 shows a very simple method for taking a sample of gas for analysis. The porcelain tube A passes through the brick-work into the flue through which the gas is carried. In the sketch a portion of the porcelain tube is cut away, to show the loose filaments of asbestos with which the tube is filled to keep dust or tarry matter from entering the burette. This asbestos must be put in very loosely, or it will pack and interfere with the free passage of the gas. Where the gas, as from a producer, etc., is constantly examined, it is very convenient to have a valve fitted permanently to an iron pipe screwed or cemented into the flue, into which the porcelain tube may be fastened by means of a rubber or asbestos * stopper. A glass tube of about ¼ inch (6 mm.) diameter is fitted into the outer end of the porcelain tube A (Fig. 100) by means of a rubber or asbestos stopper, and this glass tube is connected by means of the rubber tube C with the opening at the lower end of the burette *d*. If the gas is under pressure (as is rarely the case), it is only necessary to open the stopcocks and allow it to pass through the burette until the air is entirely displaced. Usually, however, it is necessary to draw the gas through; and the little india-rubber pump D attached to the capillary tube at the upper end of the burette is very useful for this purpose. It is fitted with a simple valve at each end, so that by compressing the bulb in the hand its contents are dis-

FIG. 100.



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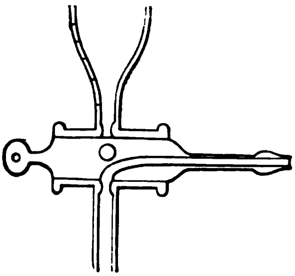
* See page 144.

charged through the outer end while the pressure closes the valve at the burette end. When the bulb is released it resumes its shape, the tension closing the outer valve and opening the one towards the burette, through which the contents of the latter are drawn into the bulb. A bulb of the usual size will empty a 100 c.c. burette in about three strokes. In taking a sample of gas, turn the three-way stopcock *b* so that the passage is open through into the burette, open the stopcock *a* at the upper end of the burette, and pump the gas through slowly for five or six minutes. Close the upper stopcock *a*, compress the rubber tube C between the thumb and fingers of the left hand, and, holding the tube with the other hand, slide the left hand towards the burette. This will compress the gas in the burette, and by closing the stopcock *b* while the tube C is thus held the gas in the burette will be under pressure. In closing *b*, it must be turned so that the passage is open from *d* out through *c*, as shown in Fig. 101. Remove the burette to the laboratory, attach the rubber tube C of the level-tube A (Fig. 103) to the end of the burette, loosen the pinchcock E, and allow the water to run through until it comes out through the rubber tube on the end of the stopcock. Close E, and allow the burette and gas to attain the temperature of the laboratory. Samples of gas for analysis may also be taken in glass tubes drawn out at the ends and closed by rubber tubes and pinchcocks or pieces of glass rod. When the sample is to be taken to a distance, it may often be collected in a metal vessel with conical ends and tubes with well-ground stopcocks. Glass vessels of the proper shape, holding from half a litre to one litre, and fitted with glass stopcocks and capillary tubes made for this purpose, may be purchased from dealers in chemical glass-ware. From these vessels or tubes the gas may be transferred to the burette by attaching to one outlet a tube filled with water and joined to the burette, likewise filled with water, placing the other end of the vessel in water, lowering the level-tube, and drawing the gas into the burette.

FIG. 101.

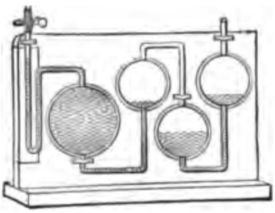


REAGENTS FOR THE PIPETTES.

Blast-furnace gas, producer gas, and, in general, gases made by drawing or forcing atmospheric air through coal or coke, contain varying amounts of carbon dioxide (CO_2), oxygen (O), carbon monoxide (CO), hydrogen (H), methane, or marsh gas (CH_4), and nitrogen (N). The best absorbents are caustic potash for carbon dioxide, pyrogallol for oxygen, and cuprous chloride in hydrochloric acid for carbon monoxide. Hydrogen is determined by ignition with excess of oxygen over palladium sponge, and marsh gas by ignition in a tube filled with cupric oxide. The pipettes required, therefore, are a simple pipette (G, Fig. 103) filled with caustic potash (1.27 sp. gr.) for absorbing carbonic acid, which is readily filled by placing in the large tube of the pipette a small glass tube, which extends down to the bottom of the bulb and is connected outside with a small glass funnel by means of a piece of rubber tubing. Pour the caustic potash in through the funnel until the large bulb of the pipette and the tube connecting the two bulbs are filled with the liquid. Draw the liquid into the capillary tube until it reaches to within a very short distance of the rubber tube on the end of the capillary, and close the rubber tube with a piece of glass tubing or a pinchcock, as shown in the sketch of the composite pipette (Fig. 102).

A composite pipette containing pyrogallol for absorbing oxygen is filled as follows. Dissolve 30 grammes of pyrogallic acid in 75 c.c. of water, attach a funnel to the capillary tube of the pipette by a piece of rubber tubing, and fill it with the solution. Attach a piece of rubber tubing to the other tube of the pipette, and by gentle suction exhaust the air; this will cause the liquid to run rapidly through the capillary tube into the pipette. Keep the funnel full until the liquid which is drawn through the large bulb into the second bulb fills the latter to an inconvenient extent, then stop the suction, and very carefully blow the liquid back into the large bulb. Fill the funnel again, and exhaust the air gently as before.

FIG. 102.



Repeat this until all the solution of pyrogallic acid has been drawn in, and then with the same precautions draw in a solution of caustic potash (1.27 sp. gr.) until the large bulb and the tube connecting the large bulb and the second bulb are filled with the liquid, which is now an alkaline solution of potassium pyrogallate. Close the capillary tube as directed for the caustic potash pipette (page 288). Insert the small tube and funnel in the large tube of the composite pipette, as directed for filling the simple pipette, and pour a little water into the last bulb of the composite pipette. The amount of water poured in should not be sufficient to fill the third bulb, for the pyrogallol rapidly absorbs the oxygen of the air in the second bulb, and this contraction causes the water poured into the last bulb to rise in the third bulb. Therefore the amount of water should be small enough to permit small bubbles of air to pass through to supply the contraction in the second bulb, and large enough to avoid emptying the third bulb when during an analysis the gas is forced through the capillary into the large bulb of the pipette. The amount of potassium pyrogallate from 30 grammes of pyrogallic acid is sufficient to absorb nearly 1500 c.c. of pure oxygen, so that a composite pipette filled in this way, and securely sealed by the water in the third and fourth bulbs, will last for a great number of analyses.

Another composite pipette for absorbing carbon monoxide is filled, as above described, with a saturated solution of cuprous chloride in hydrochloric acid (1.1 sp. gr.) and sealed with water. Each pipette should be distinctly labelled with the name of the reagent, so that no mistake can be made in using them.

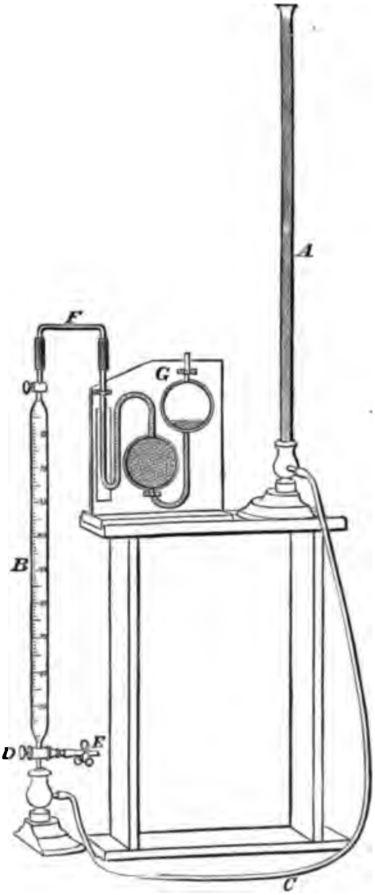
It is worthy of note that the absorption of carbon monoxide by cuprous chloride is purely mechanical, and is never absolutely perfect, so that a small amount of carbon monoxide *invariably* remains in the gas after treatment in the cuprous chloride pipette. Moreover, whenever a gas absolutely free from carbon monoxide is treated in a cuprous chloride pipette (which has previously been used to absorb carbon monoxide) and returned to the burette, it will be found to have *increased* in volume, and subsequent combustion in a palladium tube will yield an amount of carbonic acid corresponding to this increase counted as carbon monoxide. If this fact is overlooked, the carbon monoxide left in the gas will be counted as methane if a determination of this gas is made in the usual course of the analysis.

A composite pipette filled with bromine-water to absorb ethylene (C_2H_4) is sometimes used, as this gas has been found in the gases from blast-furnaces and producers using bituminous coal. But the amount of ethylene is very small, and a separate determination is rarely made, any small amount being absorbed and determined as carbon monoxide.

ANALYSIS OF THE SAMPLE.

The burette containing the gas, with the level-tube filled with water attached, as mentioned on page 287, having attained the temperature of the laboratory, raise the level-tube and open the three-way stopcock so that the passage is open for the water to enter the burette. If the gas is shown to be under a slight pressure, by raising or lowering the burette bring the water just to the stopcock (if the burette is graduated to read 100 c.c. from stopcock to stopcock, otherwise bring the water to the 0 mark), and close the stopcock. Then open the upper stopcock for an instant to allow the gas to assume the pressure of the atmosphere. Now open the three-way stopcock to allow the water to enter the burette, hold the level-tube so that the water in the tube and that in the burette are at the same level, and observe the reading of the burette. It is a very simple matter in this way to get exactly 100 c.c. of gas, which very materially simplifies the calculations. Connect the burette with the pipette containing caustic potash by means of the capillary connecting-tube, as shown in Fig. 103. Some little skill is necessary in making this connection; the best way to arrange it is as follows. Attach one end of the capillary connecting-tube to the top of the burette by a piece of rubber tubing, wiring it if necessary, then compress between the thumb and forefinger of one hand the rubber tube on the capillary of the pipette for its entire length above the pinchcock (as shown in Fig. 102), then carefully introduce the end of the capillary connecting-tube into the end of the rubber tube and release the rubber tube. If this is carefully done the walls of the rubber tube between the pinchcock and the end of the capillary will remain in contact, showing that no air has been admitted. Force the end of the capillary tube down to the pinchcock, and open the latter, allowing it to remain over the capillary as shown in Fig. 104. The apparatus will now be in the position shown in Fig. 103. Open the upper stopcock of the burette, and then turn the three-way stopcock D carefully to admit the water from the level-tube into the burette. As the water enters the burette the gas is forced over into the pipette G. Allow the water to completely fill the burette B and to enter the capillary tube F and fill it as far as the rubber connection between it and the capillary tube of the pipette G. Close the upper stopcock of the burette, place the pinchcock on the rubber tube between the capillary connecting-tube and the pipette, and remove the capillary connecting-tube F from the rubber tube of the pipette, leaving it attached to the burette. Take the pipette from the stand and shake it, to promote the absorption of the carbonic acid, which will require only a minute or two. Replace the pipette, attach the capillary connecting-tube F as before, remove the pinchcock, place the level-tube A on the floor, open the upper stopcock of the burette, and allow the water to run from the burette B into the level-tube A, drawing the gas from the pipette G into the burette B. When the caustic potash solution has run back so as to fill the large bulb and the capillary of the pipette almost to the

FIG. 103.



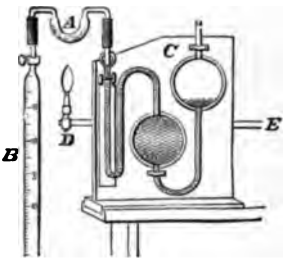
rubber connection, quickly close the upper stopcock of the burette B, replace the pinchcock on the rubber tube of the pipette G, detach the capillary connecting-tube F from the pipette, hold the level-tube A and the burette B together to get the water on an exact level, and take the reading of the burette. The difference between this reading and the original reading will be the number of c.c. of carbonic acid absorbed; and if the original reading was 100 c.c., each c.c. absorbed will be one per cent. of carbonic acid in the gas. If any other volume of gas was originally used, divide the number of c.c. absorbed by the number originally used, multiply this by 100, and the result is the percentage of carbonic acid in the gas.

If ethylene is to be determined, pass the gas into the bromine-water pipette, back into the burette, then into the caustic potash pipette to absorb any bromine fumes, finally back into the burette, and take the reading as before. The contraction is ethylene.

Now pass the gas into the pyrogallol pipette, shake the latter gently for four or five minutes to promote the absorption of the oxygen, return the gas to the burette, and note the reading. The contraction from the last reading is oxygen.

Pass the gas in the same manner into the cuprous chloride pipette, detach and shake the latter gently at short intervals for five or six minutes to promote the absorption of the carbon monoxide, return the gas to the burette, and take the reading. The contraction from the last reading is the carbon monoxide absorbed by cuprous chloride. To determine the remaining carbon monoxide and the hydrogen, the gas is mixed with oxygen and burned over spongy palladium. Fig. 104 shows the arrangement of the apparatus. A is the palladium tube, B the burette, C a pipette filled with water, D a small gas-burner for heating the palladium tube, and E the gas-pipe attached to the wood-work of the pipette and connected by a rubber tube with a supply of gas. Instead of a gas-burner for heating the palladium tube a small brass spirit-lamp may be used, which is fastened to the pipette-stand by a clamp in such a position as to bring the flame under the palladium tube. With any ordinary furnace or producer gas which contains 50 per cent. and upwards of nitrogen, the best plan is to attach an oxygen-cylinder to the top of the burette, using a capillary-tube and rubber connections, and fill the latter with oxygen gas. With water-gas, or when a supply of oxygen is not available, it is necessary to transfer a portion of the unabsorbed gas in the burette to another burette, and then to admit air to the first burette until it is nearly filled. Of course it makes the calculation a little more complicated to change the volume of the gas in this way during the progress of an analysis, but in the case of nearly pure water-gas the use of oxygen alone would probably lead to an explosion, while with other gases, in the absence of a supply of oxygen, simply filling the burette with air without letting out any of the gas might not admit enough oxygen to burn the hydrogen. After transferring a portion of the unabsorbed gas, read the burette carefully to get the volume of gas taken for combustion, and then *divide the volume of gas taken for combustion by the total volume unabsorbed, and multiply by the amount originally taken for analysis;* the result is the number of c.c. of *the original gas*, to which the amount taken for combustion corresponds.

Fig. 104.



After admitting air to the burette, which is done by standing the level-tube on the floor while the burette is on the table, opening the three-way stopcock so that the water may run into the level-tube, and opening the upper stopcock of the burette until the proper amount of air has been drawn in, take the reading of the burette with care. Connect the apparatus as shown in Fig. 104, light the gas-jet D, open the upper stopcock of the burette B, and by opening very carefully the three-way stopcock of the burette cause the gas to pass *very slowly* into the pipette C. The palladium tube should not be heated to redness, but to a temperature just below a dark-red heat. It is very necessary to avoid carrying over any water into the hot palladium tube, as it would be certain to crack it, and for this reason it is well to see that the capillary tube above the stopcock of the burette and both capillary ends of the palladium tube are dry before making the connections. Any little moisture may be removed by means of a very fine wire wrapped with thread. As the water from the combustion of the hydrogen in the palladium is liable to condense in the end of the tube near the pipette, it is always well to warm this gently with the flame of a small spirit-lamp or a piece of glowing charcoal, so as to drive all the moisture into the pipette, and thus prevent its being carried into the hot part of the palladium tube when the gas is returned into the burette. When the water has risen in the burette just above the upper stopcock, lower the level-tube and draw the gas back very slowly into the burette. When the water in the pipette has risen to the usual position in the capillary, replace the pinchcock on the rubber connection between the palladium tube and the capillary tube of the pipette, extinguish the light under the palladium tube, and, when the latter is cold, close the upper stopcock of the burette, detach the apparatus, open the three-way stopcock fully, and take the reading of the burette.

Now, if there were no carbon monoxide present in the gas before the combustion, the contraction would be due to the condensation of the water formed by the combustion of the hydrogen, and, as 2 volumes of hydrogen unite with 1 volume of oxygen to form water, $\frac{2}{3}$ of the contraction would be hydrogen. In the presence of carbon monoxide, however, there is an additional contraction beyond that caused by the formation of water, due to the fact that 2 volumes of carbon monoxide uniting with 1 volume of oxygen form 2 volumes of carbonic acid. By absorbing the carbonic acid in the caustic potash pipette, and then reading the burette, the second contraction is the volume of the carbonic acid, which is the volume of the carbon monoxide. The first contraction, then, is $\frac{3}{2}$ of the hydrogen + $\frac{1}{2}$ the carbon monoxide, and the second contraction being the volume of the carbon monoxide, it may be stated thus:

$$\text{first contraction} = \tfrac{3}{2}\ \text{hydrogen} + \tfrac{1}{2}\ \text{second contraction},$$

or

$$\tfrac{3}{2}\ \text{hydrogen} = \text{first contraction} - \tfrac{1}{2}\ \text{second contraction};$$

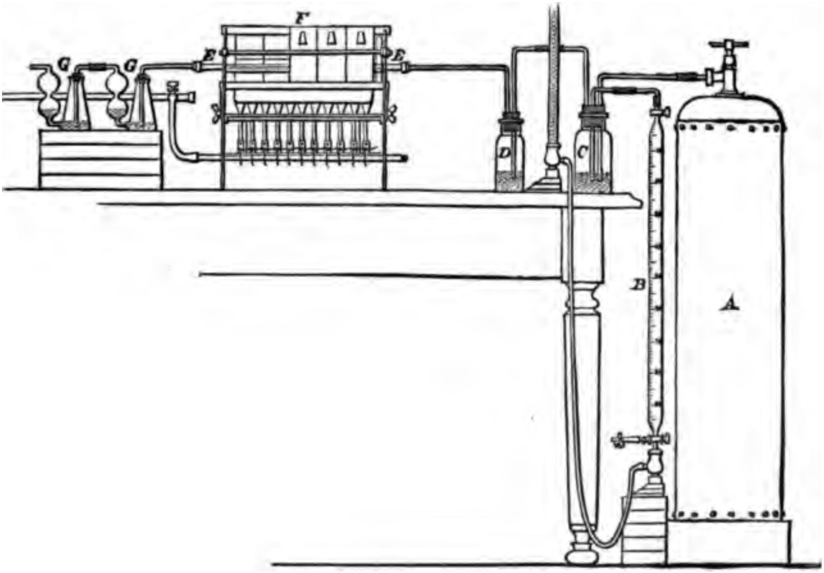
multiplying by $\frac{2}{3}$,

$$\text{Hydrogen} = \tfrac{2}{3}\ \text{first contraction} - \tfrac{1}{3}\ \text{second contraction}.$$

Divide the number of c.c. of hydrogen and carbon monoxide respectively as found above by the number of c.c. of the original gas to which the amount taken for combustion is equivalent, multiply by 100, and the result the percentage of hydrogen and carbon monoxide. This percentage carbon monoxide is to be added to the percentage found by absorption cuprous chloride, and the result is the total carbon monoxide.

There remain now in the burette only nitrogen and methane. The tter can be properly burned only at a red heat in contact with copper xide, forming water and carbonic acid. By absorbing the carbonic acid a solution of barium hydroxide, standardized by a normal solution of xalic acid, and then titrating the barium hydroxide, the volume of ethane is at once indicated. As the normal solution of oxalic acid dicates the volume of methane at 760 mm. of barometric pressure and ° C. of temperature, the thermometer and barometer must be noted, and he correction made according to the table (Table V.).

FIG. 105.



Dissolve 5.6314 grammes of crystallized oxalic acid in 1 litre of water. c.c. of this solution indicates 1 c.c. carbonic acid, or 1 c.c. methane, t 760 mm. barometric pressure and 0° C. Dissolve 14.0835 grammes of rystallized barium hydroxide in 1 litre of water. 1 c.c. of this solution is qual to about 1 c.c. of the oxalic acid solution.

The apparatus for the determination is shown in Fig. 105. It consists of a porcelain tube, EE, in the combustion-furnace F; the porcelain tube is nearly filled with coarse copper oxide between loose plugs of asbestos, or with a roll of oxidized copper wire (see page 142). The forward end is connected with two absorption-bottles, G, G, containing barium hydroxide solution. These bottles are of such a size that 25 c.c. will fill them, so that the gas in bubbling through forces a little of the solution up into the bulb-tube, thus prolonging the contact. If they are a little too large, the solution of barium hydroxide may be diluted, after it is measured in from the pipette, with a little distilled water to bring it to the proper volume. A is a cylinder containing oxygen under pressure, or, if this is not available, a couple of bottles for forcing air through the apparatus may be substituted (such as those shown in Fig. 57, page 131). The cylinder and the burette B are connected, as shown in the sketch (Fig. 105), by means of capillary tubes with the bottle C, containing caustic potash (1.27 sp. gr.). The bottle C is connected with the bottle D, containing sulphuric acid, and from D a capillary tube passes to the rubber stopper in the end of the porcelain tube EE. Start a current of oxygen or air through the apparatus (before attaching the absorption-bottles G, G), light the burners of the furnace, and raise the temperature gradually until the tube is red hot. Continue the passage of the oxygen until a bottle containing a solution of barium hydroxide attached to the end of the tube shows that no carbonic acid is given off. Measure out 25 c.c. of the barium hydroxide solution into each of the bottles G, G, and attach them as shown in Fig. 105, open the upper stopcock of the burette B, and by means of the three-way stopcock let water into the burette from the level-tube, so that the gas from the burette is made to bubble very slowly into the bottle C. About three or four bubbles should pass into C from the oxygen cylinder to one from the burette. When the water completely fills the burette and the capillary tube in C, close the upper stopcock of the burette, and continue the passage of the oxygen from A until it is certain that all the gas has been carried through the porcelain tube and the absorption-bottles. In the mean time measure out 25 or 50 c.c. of the barium hydroxide solution into a porcelain dish, dilute with water, add a drop of phenolphthalein solution (made by dissolving phenolphthalein in alcohol), and from a burette run in the standard solution of oxalic acid ~~until the~~ pink color of the solution just vanishes. This will give the value of the barium hydroxide solution in terms of the normal oxalic acid solution. When the combustion is finished, detach the absorption-bottles, wash their contents into the dish, add a drop of phenolphthalein solution, and titrate with the oxalic acid solution. The difference between the value of 50 c.c. barium hydroxide solution and that of the 50 c.c. from the absorption-bottles, in terms of the oxalic acid solution, is the number of c.c. of methane in the gas burned at 760 mm. barometric pressure and 0° C. Divide this by the number of c.c. burned, reduced to 760 mm. pressure and 0° C., multiply by 100, and the result is the volume per cent. of methane. Add together the percentages obtained of carbonic acid (ethylene, C_2H_4), oxygen, carbon monoxide, hydrogen, and methane, subtract the sum from 100, and the remainder is the percentage of nitrogen by difference.

An example will illustrate the method of analysis, thus:

EXAMPLE OF ANALYSIS.

Siemens' Producer Gas.

Volume of gas employed, 99.7 c.c.

KHO pipette	93.5 c.c.	Contraction, 6.2 c.c.		CO_2	= 6.21 %
Pyrogallol pipette	93.3 "	" 0.2 "		O	= 0.20 "
CuCl "	74.0 "	" 19.3 "	= 19.36 %	CO	
Transferred a portion.		From palladium combustion	1.42 "	CO (total)	= 20.78 "
Remaining in pipette . . .	46.8 "			H	= 11.23 "
= of original gas to . . .	63.24 "	$\left[\frac{46.8}{74}\times 99.7\right]$		CH_4	= 3.14 "
Admitted air to	98.4 "			N	= 58.44 "
					100.00 "

Burned over palladium . . 87.3 "

First contraction . . . . . 11.1 "

KHO pipette . . . . . . 86.4 "

Second contraction . . . . 0.9 " $= CO_2 = CO\left[\frac{0.9}{63.24}\times 100\right] = 1.42\%$ CO.

$H = \frac{2}{3}[11.1] - \frac{1}{3}[0.9] = 7.1$ c.c. $\left[\frac{7.1}{63.24}\times 100\right] = 11.23\%$ H.

Burned residue over oxide of copper and absorbed CO_2 in caustic baryta solution.

Thermometer 17° C. Barometer 745 mm. 745.0 — 14.4 = 730.6

7	.0086702 ×	100	= .86702
3	.0037158 ×	10	= .037158
0	×	1	= .000000
6	.0074316 ×	0.1	= .00074316
			.90492116

63.24 c.c. × .90492116 = 57.23 c.c. at 760 mm. and 0° C.

50 c.c. caustic baryta solution	= 48.3 c.c. oxalic acid
After combustion 50 c.c. " " "	= 46.5 " " "
Therefore CH_4 in gas burned	= 1.8 "

and $\frac{1.8}{57.23}\times 100 = 3.14\%$ CH_4.

TABLE I.

Atomic Weights of the Elements used in this Volume.

Name.	Symbol.	At. Wt.	Name.	Symbol.	At. Wt.
num	Al	27.07	Manganese	Mn	55.00
ony	Sb	120.00	Molybdenum	Mo	96.00
c	As	75.00	Nickel	Ni	58.70
n	Ba	137.00	Nitrogen	N	14.03
ne	Br	79.95	Oxygen	O	16.00
m	Ca	40.08	Phosphorus	P	30.97
n	C	12.00	Platinum	Pt	194.87
ne	Cl	35.45	Potassium	K	39.11
ium	Cr	52.14	Silicon	Si	28.40
	Co	59.00	Sodium	Na	23.05
r	Cu	63.40	Sulphur	S	32.06
gen	H	1.007	Tin	Sn	119.00
	I	126.85	Titanium	Ti	48.00
	Fe	56.00	Tungsten	W	184.00
	Pb	206.95	Vanadium	V	51.37
sium	Mg	24.29	Zinc	Zn	65.27

TABLE II.

Table of Factors.

Found.	Required.	Factor.	Log.
$AlPO_4$	Al	0.22181	9.3459811-10
Al_2O_3	Al	0.53005	9.7243168-10
Sb_2O_4	Sb	0.78947	9.8973356-10
Sb_2S_3	Sb	0.71390	9.8536374-10
$Mg_2(NH_4)_2As_2O_8 + H_2O$	As	0.39400	9.5954962-10
$Mg_2As_2O_7$	As	0.48297	9.6839202-10
As_2S_3	As	0.60931	9.7848383-10
As	$FeAs_2$	1.37333	0.1377749
$BaSO_4$	S	0.13756	9.1384922-10
	SO_3	0.34352	9.5359520-10
$CaSO_4$	CaO	0.41193	9.6148234-10
	$CaCO_3$	0.73513	9.8663641-10
CaO	$CaCO_3$	1.78459	0.2515385
CO_2	C	0.27273	9.4357329-10
Cr_2O_3	Cr	0.68479	9.8355574-10
$CoSO_4$	Co	0.38050	9.5803547-10
	CoO	0.48370	9.6845761-10
Co	CoO	1.27119	0.1042105
CoO	Co	0.78667	9.8957926-10
Cu	CuO	1.25240	0.0977431
	Cu_2S	1.25284	0.0978956
CuO	Cu	0.79849	9.9022695-10
Cu_2S	Cu	0.79818	9.9021008-10
Fe_2O_3	Fe	0.70000	9.8450980-10
Fe	Fe_3O_4	1.38095	0.1401779
	FeO	1.28571	0.1091430
$PbSO_4$	Pb	0.68298	9.8344080-10
	PbO	0.73578	9.8667480-10
	PbS	0.78879	9.8969614-10

TABLE II.—Continued.

Found.	Required.	Factor.	Log.
$Mg_2P_2O_7$	P	0.27836	9.4446068–10
	P_2O_5	0.63788	9.8047390–10
	MgO	0.36212	9.5588525–10
	$MgCO_3$	0.75760	9.8794400–10
Mn_3O_4	Mn	0.72052	9.8576460–10
	MnO	0.93013	9.9685437–10
$Mn_2P_2O_7$	Mn	0.38741	9.5881708–10
	MnO	0.50011	9.6990655–10
MnS	Mn	0.63175	9.8005453–10
	MnO	0.81553	9.9114399–10
$(NH_4)_3 11MoO_3PO_4$	P	0.01630	8.2121876–10
	P_2O_5	0.03735	8.5722906–10
NiO	Ni	0.78581	9.8953176–10
Ni_2S	Ni	0.78549	9.8951407–10
K_2PtCl_6	KCl	0.30696	9.4870818–10
	K_2O	0.19395	9.2876898–10
KCl	K_2CO_3	0.92690	9.9670329–10
NaCl	Na_2O	0.53077	9.7249064–10
	Na_2CO_3	0.90684	9.9575307–10
SiO_2	Si	0.47020	9.6722826–10
S	FeS_2	1.87336	0.2726212
SnO_2	Sn	0.78808	9.8965703–10
TiO_2	Ti	0.60000	9.7781513–10
V_2O_5	V	0.56222	9.7499063–10
WO_3	W	0.79310	9.8993279–10
ZnO	Zn	0.80313	9.9047858–10

TABLE III.

Percentages of P and P_2O_5 for each Milligramme of $Mg_2P_2O_7$ when 10 Grammes of the Sample are used.

Wt. of $Mg_2P_2O_7$.	P.	P_2O_5.	Wt. of $Mg_2P_2O_7$.	P.	P_2O_5.	Wt. of $Mg_2P_2O_7$.	P.	P_2O_5.	Wt of $Mg_2P_2O_7$.	P.	P_2O_5.
1	0.003	0.006	26	0.073	0.166	51	0.142	0.326	76	0.212	0.486
2	0.005	0.013	27	0.075	0.173	52	0.145	0.332	77	0.215	0.492
3	0.008	0.019	28	0.078	0.179	53	0.148	0.339	78	0.218	0.499
4	0.011	0.026	29	0.081	0.185	54	0.151	0.345	79	0.221	0.505
5	0.014	0.032	30	0.084	0.192	55	0.154	0.352	80	0.223	0.512
6	0.017	0.038	31	0.086	0.198	56	0.156	0.358	81	0.226	0.518
7	0.019	0.045	32	0.089	0.204	57	0.159	0.364	82	0.229	0.524
8	0.022	0.051	33	0.092	0.211	58	0.162	0.371	83	0.232	0.531
9	0.025	0.057	34	0.095	0.217	59	0.165	0.377	84	0.235	0.537
10	0.028	0.064	35	0.098	0.224	60	0.167	0.384	85	0.237	0.544
11	0.031	0.070	36	0.101	0.230	61	0.170	0.390	86	0.240	0.550
12	0.033	0.077	37	0.103	0.237	62	0.173	0.396	87	0.243	0.556
13	0.036	0.083	38	0.106	0.243	63	0.176	0.403	88	0.246	0.563
14	0.039	0.089	39	0.109	0.249	64	0.179	0.409	89	0.248	0.569
15	0.042	0.096	40	0.112	0.256	65	0.181	0.416	90	0.251	0.576
16	0.045	0.102	41	0.114	0.262	66	0.184	0.422	91	0.254	0.582
17	0.047	0.108	42	0.117	0.269	67	0.187	0.428	92	0.257	0.588
18	0.050	0.115	43	0.120	0.275	68	0.190	0.434	93	0.259	0.595
19	0.053	0.121	44	0.123	0.281	69	0.193	0.441	94	0.262	0.601
20	0.056	0.128	45	0.126	0.287	70	0.195	0.448	95	0.265	0.607
21	0.059	0.134	46	0.128	0.294	71	0.198	0.454	96	0.268	0.614
22	0.061	0.141	47	0.131	0.300	72	0.201	0.460	97	0.271	0.620
23	0.064	0.147	48	0.134	0.307	73	0.204	0.467	98	0.274	0.627
24	0.067	0.153	49	0.137	0.313	74	0.207	0.473	99	0.276	0.633
25	0.070	0.159	50	0.139	0.319	75	0.209	0.479	100	0.278	0.638

Tension of Aqueous Vapor in Millimetres of Mercury from 0° to 34.9° C.

°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.	°	Mm.
0.0	4.600	2.5	5.491	5.0	6.534	7.5	7.751	10.0	9.165	12.5	10.804	15.0	12.699	17.5	14.882	20.0	17.391	22.5	20.265	25.0	23.550	27.5	27.294	30.0	31.548	32.5	36.370
.1	.633	.6	.530	.1	.580	.6	.804	.1	.227	.6	.875	.1	.781	.6	.977	.1	.500	.6	.389	.1	.692	.6	.455	.1	.729	.6	.576
.2	.667	.7	.569	.2	.625	.7	.857	.2	.288	.7	.947	.2	.864	.7	15.072	.2	.608	.7	.514	.2	.834	.7	.617	.2	.911	.7	.783
.3	.700	.8	.608	.3	.671	.8	.910	.3	.350	.8	11.019	.3	.947	.8	.167	.3	.717	.8	.639	.3	.976	.8	.778	.3	32.094	.8	.991
.4	.733	.9	.647	.4	.717	.9	.964	.4	.412	.9	.090	.4	13.029	.9	.262	.4	.826	.9	.763	.4	24.119	.9	.939	.4	.278	.9	37.200
.5	.767	3.0	.687	.5	.763	8.0	8.017	.5	.474	13.0	.162	.5	.112	18.0	.357	.5	.935	23.0	.888	.5	.261	28.0	28.101	.5	.463	33.0	.410
.6	.801	.1	.727	.6	.810	.1	.072	.6	.537	.1	.235	.6	.197	.1	.454	.6	18.047	.1	21.016	.6	.406	.1	.267	.6	.650	.1	.621
.7	.836	.2	.767	.7	.857	.2	.126	.7	.601	.2	.309	.7	.281	.2	.552	.7	.159	.2	.144	.7	.552	.2	.433	.7	.837	.2	.832
.8	.871	.3	.807	.8	.904	.3	.181	.8	.665	.3	.383	.8	.366	.3	.650	.8	.271	.3	.272	.8	.697	.3	.599	.8	33.026	.3	38.045
.9	.905	.4	.848	.9	.951	.4	.236	.9	.728	.4	.456	.9	.451	.4	.747	.9	.383	.4	.400	.9	.842	.4	.765	.9	.215	.4	.258
1.0	.940	.5	.889	6.0	.998	.5	.291	11.0	.792	.5	.530	16.0	.536	.5	.845	21.0	.495	.5	.528	26.0	.988	.5	.931	31.0	.405	.5	.473
.1	.975	.6	.930	.1	7.047	.6	.347	.1	.857	.6	.605	.1	.623	.6	.945	.1	.610	.6	.659	.1	25.138	.6	29.101	.1	.596	.6	.689
.2	5.011	.7	.972	.2	.095	.7	.404	.2	.923	.7	.681	.2	.710	.7	16.045	.2	.724	.7	.790	.2	.288	.7	.271	.2	.787	.7	.906
.3	.047	.8	6.014	.3	.144	.8	.461	.3	.989	.8	.757	.3	.797	.8	.145	.3	.839	.8	.921	.3	.438	.8	.441	.3	.980	.8	39.124
.4	.082	.9	.055	.4	.193	.9	.517	.4	10.054	.9	.832	.4	.885	.9	.246	.4	.954	.9	22.058	.4	.588	.9	.612	.4	34.174	.9	.344
.5	.118	4.0	.097	.5	.242	9.0	.574	.5	.120	14.0	.908	.5	.972	19.0	.346	.5	19.069	24 0	.184	.5	.738	29.0	.782	.5	.368	34.0	.565
.6	.155	.1	.140	.6	.292	.1	.632	.6	.187	.1	.986	.6	14.062	.1	.449	.6	.187	.1	.319	.6	.891	.1	.956	.6	.564	.1	.786
.7	.191	.2	.183	.7	.342	.2	.690	.7	.255	.2	12.064	.7	.151	.2	.552	.7	.305	.2	.453	.7	26.045	.2	30.131	.7	.761	.2	40.007
.8	.228	.3	.226	.8	.392	.3	.748	.8	.322	.3	.142	.8	.241	.3	.655	.8	.423	.3	.588	.8	.198	.3	.305	.8	.959	.3	.230
.9	.265	.4	.270	.9	.442	.4	.807	.9	.389	.4	.220	.9	.331	.4	.758	.9	.541	.4	.723	.9	.351	.4	.479	.9	35.159	.4	.455
2.0	.302	.5	.313	7.0	.492	.5	.865	12.0	.457	.5	.298	17 0	.421	.5	.861	22.0	.659	.5	.858	27.0	.505	.5	.654	32.0	.359	.5	.680
.1	.340	.6	.357	.1	.544	.6	.925	.1	.526	.6	.378	.1	.513	.6	.967	.1	.780	.6	.996	.1	.663	.6	.833	.1	.559	.6	.907
.2	.378	.7	.407	.2	.595	.7	.985	.2	.596	.7	.458	.2	.605	.7	17.073	.2	.901	.7	23.135	.2	.820	.7	31.011	.2	.760	.7	41.135
.3	.416	.8	.445	.3	.647	.8	9.045	.3	.665	.8	.538	.3	.697	.8	.179	.3	20.022	.8	.273	.3	.978	.8	.190	.3	.962	.8	.364
.4	.454	.9	.490	.4	.699	.9	.105	.4	.734	.9	.619	.4	.790	.9	.285	.4	.143	.9	.411	.4	27.136	.9	.369	.4	36.165	.9	.595

TABLE V.

Table for Reducing Volumes of Gases to the Normal State.

BY PROFESSOR DR. LEO LIEBERMANN.

(From Winkler's "Technical Gas Analysis.")

Instructions for Use.

Suppose the volume of a gas to have been found = 26.2 c.c. at 742 mm. barometric pressure, 18° C. temperature, saturated with moisture. In order to reduce it to the normal state (760 mm., 0° C., dry), we proceed as follows:

1st. Look out the degree 18 (columns 1 and 4), and deduct the tension of aqueous vapor given, = 15.3 mm., from the observed pressure, = 742.0:

$$742.0 - 15.3 = 726.7 \text{ mm.}$$

2d. Now find the volume which 1 vol. of the gas would have at the pressure of 726.7 mm. by looking out seriatim the figures 7, 2, 6, and 7 in column 2 at the temperature 18°, and placing the numerical values, to be found opposite those figures, in the same column, multiplying them seriatim by 100, 10, 1, 0.1; whereupon they are added up, thus:

$$\begin{array}{llcrl} 7 & 0.0086408 & \times & 100 & = 0.86408 \\ 2 & 0.0024688 & \times & 10 & = 0.024688 \\ 6 & 0.0074064 & \times & 1 & = 0.0074064 \\ 7 & 0.0086408 & \times & 0.1 & = 0.00086408 \\ \hline & & & & 0.89703848 \end{array}$$

3d. The corrected volume of a cubic centimetre is lastly multiplied by the number of the c.c. previously found; that is, in the present case,

$$0.89703848 \times 26.2 = 23.502 \text{ c.c.}$$

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.
0	1	0.0013157		0	6	0.0078946	
0	2	0.0026315		0	7	0.0092104	
0	3	0.0039473		0	8	0.0105262	
0	4	0.0052631		0	9	0.0118420	
0	5	0.0065789	0° = 4.5				

TABLE V.—Continued.

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.
1	1	0.0013109	1° = 4.9	4	1	0.0012965	4° = 6.0
1	2	0.0026219		4	2	0.0025930	
1	3	0.0039328		4	3	0.0038895	
1	4	0.0052438		4	4	0.0051860	
1	5	0.0065548		4	5	0.0064825	
1	6	0.0078657		4	6	0.0077790	
1	7	0.0091767		4	7	0.0090755	
1	8	0.0104876		4	8	0.0103720	
1	9	0.0117986		4	9	0.0116685	
2	1	0.0013061	2° = 5.3	5	1	0.0012916	5° = 6.5
2	2	0.0026123		5	2	0.0025833	
2	3	0.0039184		5	3	0.0038750	
2	4	0.0052246		5	4	0.0051667	
2	5	0.0065307		5	5	0.0064584	
2	6	0.0078369		5	6	0.0077501	
2	7	0.0091430		5	7	0.0090418	
2	8	0.0104492		5	8	0.0103335	
2	9	0.0117553		5	9	0.0116252	
3	1	0.0013013	3° = 5.6	6	1	0.0012868	6° = 6.9
3	2	0.0026026		6	2	0.0025737	
3	3	0.0039039		6	3	0.0038606	
3	4	0.0052053		6	4	0.0051474	
3	5	0.0065066		6	5	0.0064343	
3	6	0.0078079		6	6	0.0077212	
3	7	0.0091093		6	7	0.0090080	
3	8	0.0104106		6	8	0.0102949	
3	9	0.0117119		6	9	0.0145818	

TABLE V.—Continued.

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim of mercury for ° C.
7	1	0.0012828	7° = 7.4	10	1	0.0012692	10° = 9.1
7	2	0.0025656		10	2	0.0025384	
7	3	0.0038484		10	3	0.0038076	
7	4	0.0051312		10	4	0.0050768	
7	5	0.0064140		10	5	0.0063460	
7	6	0.0076968		10	6	0.0076152	
7	7	0.0089796		10	7	0.0088844	
7	8	0.0102624		10	8	0.0101536	
7	9	0.0115452		10	9	0.0114228	
8	1	0.0012783	8° = 8.0	11	1	0.0012648	11° = 9.7
8	2	0.0025566		11	2	0.0025296	
8	3	0.0038349		11	3	0.0037944	
8	4	0.0051132		11	4	0.0050592	
8	5	0.0063915		11	5	0.0063240	
8	6	0.0076698		11	6	0.0075888	
8	7	0.0089481		11	7	0.0088536	
8	8	0.0102264		11	8	0.0101184	
8	9	0.0115047		11	9	0.0113832	
9	1	0.0012737	9° = 8.5	12	1	0.0012603	12° = 10.4
9	2	0.0025474		12	2	0.0025206	
9	3	0.0038211		12	3	0.0037809	
9	4	0.0050948		12	4	0.0050412	
9	5	0.0063685		12	5	0.0063015	
9	6	0.0076422		12	6	0.0075618	
9	7	0.0089159		12	7	0.0088221	
9	8	0.0101896		12	8	0.0100824	
9	9	0.0114633		12	9	0.0113427	

TABLE V.—Continued.

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.
13	1	0.0012559	13° = 11.1	16	1	0.0012429	16° = 13.5
13	2	0.0025118		16	2	0.0024858	
13	3	0.0037677		16	3	0.0037287	
13	4	0.0050236		16	4	0.0049716	
13	5	0.0062795		16	5	0.0062145	
13	6	0.0075354		16	6	0.0074574	
13	7	0.0087913		16	7	0.0087003	
13	8	0.0100472		16	8	0.0099432	
13	9	0.0113031		16	9	0.0111861	
14	1	0.0012516	14° = 11.9	17	1	0.0012386	17° = 14.4
14	2	0.0025032		17	2	0.0024772	
14	3	0.0037548		17	3	0.0037158	
14	4	0.0050064		17	4	0.0049544	
14	5	0.0062580		17	5	0.0061930	
14	6	0.0075096		17	6	0.0074316	
14	7	0.0087612		17	7	0.0086702	
14	8	0.0100128		17	8	0.0099088	
14	9	0.0112644		17	9	0.0111474	
15	1	0.0012472	15° = 12.7	18	1	0.0012344	18° = 15.3
15	2	0.0024944		18	2	0.0024688	
15	3	0.0037416		18	3	0.0037032	
15	4	0.0049888		18	4	0.0049376	
15	5	0.0062360		18	5	0.0061720	
15	6	0.0074832		18	6	0.0074064	
15	7	0.0087304		18	7	0.0086408	
15	8	0.0099776		18	8	0.0098752	
15	9	0.0112248		18	9	0.0111096	

TABLE V.—Continued.

Temperature ° C.	Pressure in millims. mercury	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.
19	1	0.0012301	19° = 16.3	22	1	0.0012176	22° = 19.6
19	2	0.0024602		22	2	0.0024352	
19	3	0.0036903		22	3	0.0036528	
19	4	0.0049204		22	4	0.0048704	
19	5	0.0061505		22	5	0.0060880	
19	6	0.0073806		22	6	0.0073056	
19	7	0.0086107		22	7	0.0085232	
19	8	0.0098408		22	8	0.0097408	
19	9	0.0110709		22	9	0.0109584	
20	1	0.0012259	20° = 17.4	23	1	0.0012135	23° = 20.9
20	2	0.0024518		23	2	0.0024270	
20	3	0.0036777		23	3	0.0036405	
20	4	0.0049036		23	4	0.0048540	
20	5	0.0061295		23	5	0.0060675	
20	6	0.0073554		23	6	0.0072810	
20	7	0.0085813		23	7	0.0084945	
20	8	0.0098122		23	8	0.0097080	
20	9	0.0110331		23	9	0.0109215	
21	1	0.0012218	21° = 18.5	24	1	0.0012094	24° = 22.2
21	2	0.0024436		24	2	0.0024188	
21	3	0.0036654		24	3	0.0036282	
21	4	0.0048872		24	4	0.0048376	
21	5	0.0061090		24	5	0.0060470	
21	6	0.0073308		24	6	0.0072564	
21	7	0.0085526		24	7	0.0084658	
21	8	0.0097744		24	8	0.0096752	
21	9	0.0109962		24	9	0.0108846	

TABLE V.—Continued.

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.	Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aq. vapor in millim. of mercury for ° C.
25	1	0.0012054		28	1	0.0011933	
25	2	0.0024108		28	2	0.0023866	
25	3	0.0036162		28	3	0.0035799	
25	4	0.0048216		28	4	0.0047732	
25	5	0.0060270	25° = 23.5	28	5	0.0059665	28° = 28.1
25	6	0.0072324		28	6	0.0071598	
25	7	0.0084378		28	7	0.0083531	
25	8	0.0096432		28	8	0.0095464	
25	9	0.0108486		28	9	0.0107397	
26	1	0.0012013		29	1	0.0011894	
26	2	0.0024026		29	2	0.0023788	
26	3	0.0036039		29	3	0.0035682	
26	4	0.0048052		29	4	0.0047576	
26	5	0.0060065	26° = 25.0	29	5	0.0059470	29° = 29.8
26	6	0.0072078		29	6	0.0071364	
26	7	0.0084091		29	7	0.0083258	
26	8	0.0096104		29	8	0.0095152	
26	9	0.0108117		29	9	0.0107046	
27	1	0.0011973		30	1	0.0011855	
27	2	0.0023946		30	2	0.0023710	
27	3	0.0035919		30	3	0.0035565	
27	4	0.0047892		30	4	0.0047420	
27	5	0.0059865	27° = 26.5	30	5	0.0059275	30° = 31.6
27	6	0.0071838		30	6	0.0071130	
27	7	0.0083811		30	7	0.0082985	
27	8	0.0095784		30	8	0.0094840	
27	9	0.0107757		30	9	0.0106695	

INDEX.

PAGE

Absorption apparatus for carbon dioxide in carbon determinations 144
  precautions in weighing 146
Acetic acid, reagent 40
Acids and halogens 38
Air, compressed, for use in carbon determinations in iron and steel 155
Air-bath 19
Air-blast with Richards's injector 24
Alcohol lamps 23
Alkalies, determination of, in clay 267
  determination of, in iron ores 252
Alkaline earths, salts of 51
  salts 44
Allen, determination of nitrogen in iron and steel 200
Alumina and ferric oxide, separation of . . 245
  by ammonium sulphide . . 245, 264
  by caustic potash or soda 246
  by sodium hyposulphite . . 193, 247
  by volatilization of the iron in a current of hydrochloric acid gas after reduction by hydrogen 247
Aluminum, determination of, in iron and steel 191
  Carnot's method 192
  ether method 193
  Stead's method 191
  separation of, from chromium . . 189, 193
Ammonia, reagent 44
Ammonium acetate, reagent 45
  bisulphite, reagent 44
  chloride, reagent 45
  fluoride, reagent 45
  nitrate, reagent 45
  oxalate, reagent 46
    quantity required in the determination of lime in limestone . . 262

PAGE

Ammonium sulphide, reagent 44
  salts, decomposition of, by nitric acid 253
Apparatus 11
  general laboratory 18
Arsenic, determination of, as arsenious sulphide 194
  as magnesium arsenate 195
  by distillation 194
  in iron and steel 194
Arsenic and antimony, separation of, from copper and lead 250
Arsenic, copper, antimony, and lead, determination of, in iron ores 249
Asbestos stoppers 144
Ash in coal and coke, determination of . . 278

Babbitt, use of red lead in Deshays's method for determination of manganese in iron and steel 122
Balances 35
Bamber's method for sulphur in pig-iron . 67
Barba, asbestos for settling carbonaceous matter in solutions of steel 151
  determination of chromium in steel . 190
  member of Sub-Committee on Methods 92
Barium acetate, reagent 51
  carbonate, reagent 51
  chloride, reagent 51
  determination of, as sulphate in iron ores 238
  hydroxide, reagent 52
Baryta, caustic, reagent 52
  caustic, standard solution of, for determination of methane 295
Berzelius, determination of carbon in iron and steel 127
  determination of sulphur in iron and steel 63

PAGE
Binks, determination of carbon in iron and steel 127
Boat of platinum-foil for determination of carbon in iron and steel 158
Boats of platinum for determination of carbon in ferro-chrome 133
Britton, permanent standards for color-carbon method 177
Bromine, reagent 40
Bromine-water for absorbing ethylene . . 292
Bunsen burners 21
    chimneys for 22
Bunsen, determination of manganese dioxide in iron ores 234
Bunsen's method of rapid filtration . . . 25

Calcium carbonate, reagent 52
    chloride, reagent 52
Camera, for use in color-carbon method . 176
Caps for reagent bottles 31
Carbon, determination of, in ferro-chrome . 132
    in iron and steel 126
    in carbonaceous matter, determination of, in iron ores 255
Carbon, combined, determination of, in iron and steel by color method . . 170
    determination of, in white cast iron and pig-iron 178
        by direct method 170
        by indirect method 170
    limitations of color method . . . 171
Carbon, fixed, determination of, in coal . 278
Carbon, total, determination of, in iron and steel 126
    by combustion with copper oxide in a current of oxygen 131
    by combustion with lead chromate and potassium chlorate . . . 129
    by combustion with potassium bisulphate 132
    by direct combustion in oxygen . 128
    by solution and oxidation of the borings by sulphuric, chromic, and phosphoric acids, the carbon dioxide being measured . 137
    by solution and oxidation of the borings by sulphuric, chromic, and phosphoric acids, the carbon dioxide being weighed . . 140

PAGE
Carbon, total, determination of, by solution in copper chloride, and combustion of residue 165
    by solution in copper sulphate, and combustion of residue by chromic and sulphuric acids . . 168
    by solution in cupric sulphate, and combustion of residue in a current of oxygen 167
    by solution in dilute hydrochloric acid in an electric current, and combustion of residue 168
    by solution in iodine or bromine, and combustion of residue . . 165
    by solution on fused silver chloride, and combustion of residue . 166
    by solution in potassium-cupric chloride, and combustion of residue 148
        modification of (Job and Davies) 160
    by volatilization in a current of chlorine, and combustion of residue 142
    by volatilization in a current of hydrochloric acid gas, and combustion of residue 148
Carbonic acid gas, reagent 42
    absorbent for 288
    apparatus for generating 61
    determination of, in gases . . . 290
    determination of, in iron ores . . 253
    purifying and drying apparatus for, in carbon determinations 144, 155
Carbonic oxide gas, absorbent for 289
    absorption of, by cuprous chloride 289
    determination of, in gases . 292, 294
Carnot, determination of aluminum in iron and steel 192
    determination of nickel in steel . . . 186
Centrifugal machine 122
Chase, determination of nickel 186
Chimneys for Bunsen burners 22
Chlorine, reagent 41
Chrome iron ore, analysis of 259
Chromic acid, reagent 42
Chromium, determination of, in ferro-chrome 208

PAGE
Chromium, determination of, in iron and steel 188
    ether method 189
  determination of, in iron ores 258
  separation of, from aluminum 189, 193, 259
  volumetric method for determination of, in iron and steel 189
Chromium and aluminum, separation of, from phosphoric acid 259
Cinder, mill and tap, analysis of 273
Citric acid, reagent 40
Clay, methods for the analysis of 266
Coal, calorific power of 283
  determination of sulphur in 278
  heating effect of 283
  proximate analysis of 276
  ultimate analysis of 282
Coal and coke, methods for the analysis of 276
Cobalt, determination of, as sulphate . . . 184
  determination of, by electrolysis . . . 185
Cobalt and nickel, determination of, in iron and steel 183
Coke, determination of sulphur in 278
Combined water, determination of, in iron ores 255
Committee on Coal Analysis, reference to . 276
Comparison-tubes for color-carbon method . 175
Cone, Gooch's perforated 28
Copper, determination of, as cupric oxide . 183
    as cuprous sulphide 183
    by electrolysis 180
    by precipitation by sodium hyposulphite 182
  anhydrous sulphate, reagent 53
  metallic, reagent 53
  oxide, reagent 55
  sulphate, reagent 53
Copper and ammonium, double chloride of, reagent 54
  and potassium, double chloride of, reagent 54
    repeated use of, for solution of iron and steel 164
Copper, lead, arsenic, and antimony, determination of, in iron ores 249
Counterpoised filters 28
Craig, determination of sulphur in iron and steel 65
Crucibles 32

PAGE
Crucibles, Gooch's perforated 27
Crucible-tongs, forms of 34
Cupric chloride, reagent 54
Cuprous chloride, anhydrous, reagent . . 54
    reagent, for absorbing carbon monoxide 289

Davies, carbon in iron and steel 160
Deshays, determination of manganese in iron and steel 121
Desiccators 32
Deville, determination of carbon in iron and steel 127
Dishes, platinum 33
Distilled water 37
  apparatus for making 37
Drill-press 15
Drill-press for holding half a pig of iron . 15
Drill-press and balance 16
Drown, determination of silicon in pig-iron 73
  determination of sulphur in iron and steel 65
  determination of titanium in iron . . 180
  member of Sub-Committee on Standard Methods 92
Drying and purifying apparatus for carbon dioxide in carbon determinations . 144, 145
Dubois and Mixer, determination of iron in iron ores 217
Dudley, chairman Sub-Committee on Standard Methods 92

Eggertz, determination of carbon in iron and steel 127
  determination of combined carbon in iron and steel 170
  determination of phosphorus in iron and steel 90
Elliott, determination of sulphur in iron and steel 68
Eschka, determination of sulphur in coal and coke 279
Ethylene, absorbent for 290
  determination of, in gases 292

Factor weights 36
Feather for removing precipitates 31
Ferric chloride, solution of, for standardizing solutions of permanganate and bichromate 218

PAGE
Ferro-chrome, determination of carbon in . 132
Ferrous oxide, determination of, in iron ores 221
Ferrous sulphate, reagent 56
Ferrous-ammonium sulphate, reagent . . 56
Filtering-tubes for carbon determinations in iron and steel 156
Filter-paper 29
Filter-pumps 24
Filters, ashless 29
Filtration, Bunsen's method of 25
Fire-sands, method for analysis of 275
Forceps for use in carbon determinations in iron and steel 153
Ford, determination of manganese in iron and steel 113
 rapid method for determination of silicon in pig-iron 77
Fresenius, determination of phosphorus in iron and steel 80
 determination of sulphur in iron and steel 64

Galbraith, volumetric method for determination of chromium in iron and steel . . 189
Gas, Siemens's producer, example of analysis of 298
Gases, analysis of, by Hempel's apparatus 290
 collecting samples of, for analysis . . 285
 methods for the analysis of 285
 reagents 42, 288
Glass filtering-tube for carbon determinations in iron and steel 156
Gooch, separation of titanic acid and alumina 229
Gooch's method of rapid filtration 27
 perforated crucible and cone 27
 tubulated crucible 256
Graphitic carbon, determination of, in iron and steel 169

Handy, determination of phosphorus in iron and steel 104
Hempel's apparatus for the analysis of gases 285
Hogarth, specific-gravity flask 261
Hydrochloric acid, reagent 38
Hydrofluoric acid, apparatus for distilling . 39
 reagent 39
Hydrogen, combustion of, with spongy palladium 292
 gas, apparatus for generating 61
Hydrogen sulphide gas 43
 apparatus for generating 61
Hygroscopic water, determination of, in iron ores 211

Igniting precipitates 22
Insoluble silicious matter in iron ores, analysis of 237
Iodine, reagent 41
Iron, determination of, in ferro-chrome, ferro-silicon, and ferro-titanium . . 209
 determination of metallic, in iron and steel 203
Iron, total, determination of, in iron ores . 212
 by deoxidation by ammonium bisulphite 215
 by deoxidation by stannous chloride 216
 by deoxidation by zinc . . . 213
 by standard solution of potassium bichromate 214
 by standard solution of potassium permanganate . . . 214
Iron ores, method of sampling 210
Iron wire, reagent 55
Iron and ammonium, double sulphate of, reagent 56

Job, carbon in iron and steel 160

Karsten, determination of graphitic carbon in pig-iron 169
 determination of sulphur in iron and steel 60
Kudernatsch, determination of carbon in iron and steel 127

Langley, determination of carbon in iron and steel 127
 determination of nitrogen in iron and steel 201
Lead, determination of, as lead sulphate in iron ores 250
 chromate, reagent 57
 oxide, dissolved in caustic potash . . 58
 peroxide, reagent 57

PAGE

- Lead, copper, arsenic, and antimony, determination of, in iron ores 249
- Limestone, methods for the analysis of 262
  - occasional constituents of 263
- Lundin, determination of arsenic in iron and steel 194

- Magnesia, determination of, in iron ores 238
  - in limestones 263
- Magnesia-mixture, reagent 59
- Manganese, dioxide of, in iron ores 233
  - determination of, by Bunsen's method 234
    - by ferrous sulphate method 235
  - determination of, as manganese pyrophosphate 111
    - as manganoso-manganic oxide 111
    - as manganous sulphide 112
  - determination of, in ferro-chrome, ferro-silicon, and ferro-titanium 208
  - determination of, in iron and steel, by acetate method 108
    - by Deshays's method 121
      - Vanier's modification 122
    - by Ford's method 113
    - by nitric acid and potassium chlorate method 113
    - by Volhard's method 116
    - by Williams's method 118
    - in presence of much silicon (Wood's method) 115
    - rapid methods 116
    - remarks on the use of acetate method 112
  - determination of, in iron ores 230, 248
    - by Pattinson's method 232
    - by Volhard's method 232
  - determination of, in pig-iron, spiegel, and ferro-manganese, by Ford's method 115
  - determination of, in spiegel and ferro-manganese 120
    - by Pattinson's method 123
    - by Williams's method 120
  - determination of, in steel, by the color method 124
    - in presence of much silicon (Ford's method) 115

PAGE

- Marguerite's method for determination of iron 214
- Matthewman, determination of sulphur in pig-iron 67
- Measuring-glasses for reagents 31
- Mercuric oxide, reagent 57
- Mercurous nitrate, reagent 56
- Metals and metallic salts, reagents 53
- Methane, determination of, in gases 295
- Microcosmic salt, quantity necessary in the determination of magnesia in limestones 263
  - reagent 46
- Mixer and Dubois, determination of iron in iron ores 217
- Moisture in coal, determination of 276
- Molybdate solution, reagent 59, 97
- Molybdenum, determination of, in ferro-molybdenum 200
  - determination of, in iron and steel 199
- Morrell, determination of sulphur in iron and steel 63
- Mortar, agate, with Stow flexible shaft 13
  - agate, White's arrangement to use with power 14
  - hardened steel, for spiegel 17
- Mortar and pestle, steel, for crushing ores 12
- Muffles 23

- Nessler, reagent for nitrogen determinations 201
- Nichols, details of rapid method for determination of phosphorus in iron and steel 106
- Nickel, determination of, as nickel sulphide or nickel oxide 185
  - determination of, by ether method 186
  - separation of, from cobalt 184
- Nickel and cobalt, determination of, by electrolysis 185
  - determination of, in iron and steel 183
  - separation of, from copper 184
- Nickel, cobalt, zinc, and manganese, determination of, in iron ores 248
- Nickel steel, analysis of 185
- Nitric acid, reagent 38
- Nitrogen, determination of, in gases 297
  - determination of, in iron and steel 200

PAGE

Oxalic acid, reagent 40
  standard solution of, for determination of methane 295
Oxygen, absorbent for 282
  determination of, in gases 292
  gas, reagent 43

Pan, aluminum, for weighing samples . . 36
Penny's method for determination of iron 214
Perforated boat and holder for filtering carbonaceous residues from iron and steel . 151
Permanent standards for color-carbon determinations 177
Peters, determination of manganese in steel by color method 124
Phillips, determination of sulphur in pig-iron 67
Phosphoric acid, determination of, in coal and coke 281
  in iron ores 227
  in limestone 264
  in slags 274
Phosphorus, determination of, in ferro-chrome 207
  in ferro-silicon 207
  in ferro-titanium 208
  in iron and steel 80
    alkalimetric method 104
    by direct weighing of phospho-molybdate 106
    by the acetate method . . . 80
    by the acetate method, precautions necessary . . 82, 84
    by the combination method . 91
    by the molybdate method . 88
    by the molybdate method, precautions necessary . 91, 92
    by the volumetric method (method of the Sub-Committee on Methods of the International Steel Standards Committee) 92
    by rapid methods 92
      when titanium is present 85, 92
    as ammonium phospho-molybdate 91
    as magnesium pyrophosphate 85
  in iron and steel, as magnesium pyrophosphate with previous precipitation as phospho-molybdate 90
  separation of, from arsenic 82, 91
Phospho-titanate, insoluble 85
Pichard, determination of manganese in steel by the color method 124
Pipette, Hempel's composite, method of filling 289
  Hempel's simple, method of filling . 288
Plate, chilled iron, and muller 12
Platinic chloride solution, reagent 58
Platinum apparatus 32
  combustion-tube for carbon determinations in iron and steel 153
    in ferro-chrome 133
  crucibles, method of cleaning 32
  filtering-tube for carbon determinations in iron and steel 156
"Policemen" for removing precipitates . . 31
Potash and soda, separation of 252
Potassium bichromate, reagent 48
  bisulphate, reagent 49
  chlorate, reagent 49
  ferricyanide, reagent 50
  ferrocyanide, reagent 50
  hydroxide, reagent 47
  iodide, reagent 50
  nitrate, reagent 48
  nitrite, reagent 47
  permanganate, reagent 50
  sulphide, reagent 48
Potassium permanganate solution, methods of standardizing 96, 217
  standard solution of, for determination of iron 221
Potassium pyrogallate, absorbent power of 289
Purifying apparatus for oxygen and air . . 144

Rack for permanent standards in color-carbon method 178
Rapid evaporations, apparatus for 20
Rapid filtration, Bunsen's method of . . . 25
  Gooch's method of 27
Reagents 37
  for determining phosphorus 59
  for the analysis of gases 288
Reductor, simple form of 94

PAGE
Regnault, determination of carbon in iron and steel 127
Removing precipitates from beakers . . . 30
Richards injector 24
Richter, determination of carbon in iron and steel 127
Riley, determination of titanium in pig-iron 179
Rivot, separation of alumina and ferric oxide 247
Rose, separation of alumina and ferric oxide 246
Rothe, determination of nickel in steel . . 186
  determination of chromium in steel . 188
Rubber stoppers 32

Safety-guard tube in carbon determinations 145
Sampling iron ores, method of 210
  pig-iron, method of 15
Sand-bath 18
Sargent, rechlorinated double chloride solution 164
Shimer, member Sub-Committee on Standard Methods 92
  insolubility of titanium carbide in hydrochloric acid 170
Siemens's producer gas, example of analysis of 298
Silica, determination of, in iron ores . 237, 244
Silica, alumina, lime, magnesia, manganese oxide, and baryta, determination of, in iron ores 236
Silicon, determination of, in ferro-silicon, ferro-chrome, etc. 206
  determination of, in iron and steel . . 72
    by solution in nitric and hydrochloric acids 72
    by volatilization in a current of chlorine 73
  determination of, in pig-iron, Drown's method 73
  rapid method, by Ford 77
Slag and oxides, determination of, in iron and steel 78
    by solution in iodine 78
    by volatilization in a current of chlorine gas 80
Slag, basic, analysis of 273
  converter, analysis of 273

PAGE
Slag decomposed by hydrochloric acid, analysis of 271
  not decomposed by hydrochloric acid, analysis of 273
Slag refinery, analysis of 273
Slags, methods for the analysis of 271
Smith, J. L., determination of alkalies in minerals 268
Soda and potash, separation of 252
Sodium acetate, reagent 47
  carbonate, reagent 46
  hyposulphite, reagent 47, 69
  nitrate, reagent 47
  thiosulphate, reagent 47, 69
Sodium-ammonium phosphate, reagent . . 46
Sodium hydroxide, reagent 46
Sonnenschein, determination of phosphorus in iron and steel 88
Spatulas, platinum 34
Specific gravity of iron ores, method of determining 260
    flask for 261
Stand for holding absorption apparatus for carbon dioxide in the determination of carbon in iron and steel 146
Standard solutions for determination of iron, proper strength of 221
Standardizing volumetric solutions for determination of iron by ferrous sulphate 220
    by iron wire 96, 220
    by solution of ferric chloride . . 218
Starch solution, reagent 69
Stead, determination of aluminum in iron and steel 191
Stirring machine for dissolving steel and iron in carbon determinations 149
Sulphates, soluble, determination of, in iron ores 226
Sulphur, conditions of, in coal 281
  as sulphides, in iron ores 225
  determination of, in ferro-chrome, ferro-silicon, and ferro-titanium . . 205
  determination of, in iron and steel by evolution as hydrogen sulphide 60
    by evolution as hydrogen sulphide and absorption by alkaline solution of lead nitrate 60

PAGE

- Sulphur, determination of, in iron and steel
  - by evolution as hydrogen sulphide and absorption by ammoniacal solution of cadmium sulphate 63
  - by evolution as hydrogen sulphide and absorption in ammoniacal solution of silver nitrate 63
  - by evolution as hydrogen sulphide and absorption and oxidation by bromine and hydrochloric acid 64
  - by evolution as hydrogen sulphide and absorption and oxidation by hydrogen peroxide 65
  - by evolution as hydrogen sulphide and absorption and oxidation by potassium permanganate 65
  - by rapid method 68
  - determination of, in coal and coke 278
  - determination of, in pig-iron, Bamber's method 67
    - special precautions 67
  - total, determination of, in iron ores 225
    - method of reporting amount of, in coal 281
- Sulphuric acid, reagent 39
- Sulphurous acid, reagent 41
- Svanberg and Struve, phospho-molybdate reaction 88

- Tartaric acid, reagent 40
- Tin, determination of, in iron and steel 195
- Titanic acid, determination of, in clay 269
  - determination of, in iron ores 229
  - interference of phosphoric acid with precipitation of 229
  - iron ores containing 228
    - analysis of 228
  - separation of, from phosphoric acid 229
  - tests for, in iron ores 228
- Titaniferous iron ores, method of recognizing 228
- Titanium, determination of, in iron 179
  - by precipitation 179
  - by volatilization 180
- Triangles and tripods of platinum 34
- *Tripods* 22

PAGE

- Tungsten, determination of, in iron and steel 196
  - in iron ores 260
  - rapid method for determination of, in iron and steel 197

- Uehling, apparatus for delivering constant volumes of ferrous sulphate solution 120
  - apparatus for delivering different volumes of nitric acid 173
- Ullgren, determination of carbon in iron and steel 127

- Vanadium, determination of, in iron and steel 197
  - determination of, in iron ores 260
- Volatile combustible matter in coal, determination of 277
- Volhard, determination of manganese in iron and steel 116
  - in high grade manganese ores 232

- Washing-bottles, forms of 29
- Watch-glasses, balanced 36
- Water of composition, determination of, in clays 269
  - in iron ores 255
- Water-bath, for determination of hygroscopic water in iron ores 211
  - for use in color-carbon method and color-manganese method 172
- Watts, determination of silicon in iron and steel 75
- Weyl, determination of carbon in iron and steel 127
- Whitfield, apparatus for hastening evaporations 20
- Williams, method for determination of manganese in iron and steel 118
- Wöhler, determination of carbon in iron and steel 127
  - separation of alumina and ferric oxide 247
- Wood, modification of color-carbon method for low steels 175
  - modification of rapid method for sulphur in iron and steel 71
  - rapid method for determination of phosphorus in iron and steel 106

PAGE
Wood, use of hydrofluoric acid in steels high in silicon, and in pig-irons, in determination of manganese 115

Zimmerman, determination of iron in iron ores 216

PAGE
Zinc, determination of, in iron ores . . . 248
  metallic, reagent 58
    amalgamated for use in reductor . 97
    powdered for reducing molybdic acid 99
  oxide in water, reagent 58

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